# Broadening of the Proton Magnetic Resonance Spectra of Sulfonate Anions by Ion Pairing with Paramagnetic Chromium(III) Complexes

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The paramagnetic line broadening of both the $^1$H spectra of $CH_3SO_3^-$ and $(CH_2SO_3)_2^{2-}$ was observed in aqueous solutions including chromium(III) complexes such as $[Cr(en)_3]^{3+}$ (en=ethylenediamine), $[Cr(phen)_3]^{3+}$ (phen=1,10-phenanthroline), and *lel,lel,lel*-$[Cr(chxn)_3]^{3+}$ (chxn=*trans*-1,2-cyclohexanediamine). The dependence of the line broadening on the concentration of chromium(III) complexes was attributed to contact ion-pair formation. The distances between the Cr atom and the H atoms of the anions in contact ion pairs were derived in order to discuss their configurations. The anions were considered to be in contact with the complex ions through one or two sulfonate groups directed toward the Cr atom in the open space along the $C_3$-axis of the complex or in hollow regions between the ligands.

The formation of ion pairs between the metal complex cations and the various anions was previously studied using conductivity measurements.[1] The differences between the experimental and theoretical ion-pair formation constants were attributed to the presence of such interactions as the hydrophobic type and hydrogen bonding between the metal complex cations and the anions.

Nuclear magnetic resonance spectroscopy has provided a powerful tool for studying the microdynamic behavior of ions in solution.[2,3] If one of the ions in an ion pair is paramagnetic, the diamagnetic counterions will experience a magnetic field caused by that paramagnetic ion. This paramagnetism on the counterion produces an NMR spectrum that is either a resonance shift, line broadening, or both. From such a spectrum we can obtain configurational information concerning the ion pair.[4] Paramagnetic line-broadening of the diamagnetic ion is related to the dynamic behavior of the ion pair. In the simplest case of isotropic reorientational motion, the dipolar contribution of a paramagnetic ion to the line width, $(\Delta\nu_{1/2})_{IP}$ in Hz, or the transverse relaxation time, $T_2$, for the proton is expressed as[4,5]

$$\pi(\Delta\nu_{1/2})_{IP} = (T_2^{-1})_{IP} = J\tau_C r_{CrH}^{-6}[7 + 13/(1 + \omega_S^2\tau_C^2)]/15. \quad (1)$$

For the present system, $\tau_C$ is the dipolar correlation time, $\omega_S$ the electron spin resonance frequency, and $r_{CrH}$ the electron-nuclear distance corresponding to the distance between the chromium(III) atom of the complex and the hydrogen atoms of the anion within the ion pair.

The parameter $J$ is given by

$$J = S(S + 1)\gamma_H^2 g^2 \beta^2, \quad (2)$$

where $S$ is the total electron spin of Cr(III), $\gamma_H$ is the nuclear gyromagnetic ratio of proton, and $g$ and $\beta$ are the $g$-factor for the magnetic moment and the Bohr magneton of electron spin in Cr(III), respectively. In the present study, the paramagnetic line-broadening of the hydrogen atoms of $CH_3SO_3^-$ or $(CH_2SO_3)_2^{2-}$ was observed in the presence of chromium(III) complex cations and was analyzed by considering their ion-pair formations. The values of $r_{CrH}$ given in Eq. 1 were estimated through $(\Delta\nu_{1/2})_{IP}$ based on some assumptions; the configurations of the ion pairs are discussed.

## Experimental

The $^1$H NMR measurements were performed using a JEOL GX-270 Fourier-transform spectrometer operating at 270.0 MHz with 5-mm (diameter) tubes at 27 °C on aqueous solutions of sodium salt of $CH_3SO_3^-$ or $(CH_2SO_3)_2^{2-}$ of 0.0100 mol dm$^{-3}$ in the presence of chlorides of the Cr(III) complexes while changing their concentrations from 0.00600 to 0.0200 mol dm$^{-3}$. The preparation of the salts used was proviously described.[1]

## Results and Discussion

The $^1$H NMR spectra of both the $CH_3SO_3^-$ and $(CH_2SO_3)_2^{2-}$ ions were single lines with widths less than 1 Hz; they were assigned to the methyl and the methylene protons, respectively. The observed half widths, $(\nu_{1/2})_{obsd}$, depended on the concentrations of the chromium(III) complexes, while the chemical shifts did not. The concentration dependence of the half width can be attributed to the ion-pair formation of the anions with chromium(III) complexes.[4] In the present study we assumed that a formed ion pair could be classified into a solvent-separated ion pair and a contact type in a similar manner as before.[6] The equilibria for the ion-pair formations are expressed by

$$M+A \rightleftharpoons MA(sep) \rightleftharpoons MA(con), \quad (3)$$

where M is the free complex ion, A the free anion, MA(sep) the solvent-separated ion pair, and MA(con) the contact ion pair. Since the relaxation time for the exchange of anions between free and ion-pairing types is sufficiently shorter than $T_2$, the observed half width change, $(\Delta\nu_{1/2})_{\mathrm{obsd}}$, can be written as

$$\begin{aligned}(\Delta\nu_{1/2})_{\mathrm{obsd}} &= (\nu_{1/2})_{\mathrm{obsd}} - (\nu_{1/2})_0 \\ &= [P_{\mathrm{A}}(T_2{}^{-1})_{\mathrm{A}} + P_{\mathrm{MA(sep)}}(T_2{}^{-1})_{\mathrm{MA(sep)}} \\ &\quad + P_{\mathrm{MA(con)}}\,(T_2{}^{-1})_{\mathrm{MA(con)}}]/\pi,\end{aligned} \tag{4}$$

where $(\nu_{1/2})_0$ is the half width in a sodium sulfonate solution having no complex ion and $P$ is the fraction of each species in solution. Since terms including $(T_2{}^{-1})_{\mathrm{A}}$ and $(T_2{}^{-1})_{\mathrm{MA(sep)}}$ are presumed to be negligible, since the distance between the Cr(III) atom of the complex and the H atoms of the free anions or of the anions in the solvent-separated ion-pair should be considerably larger than that in the contact ion pair ($r_{\mathrm{MA(con)}}$), we approximate Eq. 4 as

$$\begin{aligned}(\Delta\nu_{1/2})_{\mathrm{obsd}} &= P_{\mathrm{MA(con)}}(T_2{}^{-1})_{\mathrm{MA(con)}}/\pi \\ &= P_{\mathrm{MA(con)}}(\Delta\nu_{1/2})_{\mathrm{MA(con)}} \\ &= (1-P_{\mathrm{A}})x_{\mathrm{MA(con)}}(\Delta\nu_{1/2})_{\mathrm{MA(con)}},\end{aligned} \tag{5}$$

where the fact that $1-P_{\mathrm{A}}$ is identical to $P_{\mathrm{MA(sep)}}+P_{\mathrm{MA(con)}}$, and $x_{\mathrm{MA(con)}}$ means that the fraction of contact ion pairs out of the total number of ion pairs, which is equivalent to $[\mathrm{MA(con)}]/\{[\mathrm{MA(sep)}]+[\mathrm{MA(con)}]\}$ or $P_{\mathrm{MA(con)}}/(1-P_{\mathrm{A}})$.

The values of $P_{\mathrm{A}}$ for each solution can be evaluated by using the ion-pair formation constant ($K$) obtained on the basis of the usual thermodynamic methods. For the present ion-pair systems, the concentration equilibrium constants ($K_{\mathrm{c}}$),

$$K_{\mathrm{c}} = ([\mathrm{MA(sep)}] + [\mathrm{MA(con)}])/([\mathrm{M}][\mathrm{A}]), \tag{6}$$

were determined from conductivity measurements under an ionic strength ($I$) of 0.01 at 25 °C;[1] the values of $K_{\mathrm{c}}$ are summarized in Table 1. Although the present study was carried out at 27 °C, these $K_{\mathrm{c}}$ values were used without any correction. The $P_{\mathrm{A}}$ values, however, were calculated by correcting $K_{\mathrm{c}}$ for the difference in the ionic strength with the Debye-Hückel equation[1,7] for the activity coefficients of ions and also by considering the effect of ion-pair formation of the complex ion with coexisting chloride ions. The values of $P_{\mathrm{A}}$, thus obtained, are shown in Table 2, together with those of $(\Delta\nu_{1/2})_{\mathrm{obsd}}$.

Using the concentration equilibrium constant for the solvent-separated ion-pair formation,

$$K_{\mathrm{c(sep)}} = [\mathrm{MA(sep)}]/([\mathrm{M}][\mathrm{A}]), \tag{7}$$

we can express $x_{\mathrm{MA(con)}}$ in Eq. 5 as

$$x_{\mathrm{MA(con)}} = 1 - K_{\mathrm{c(sep)}}/K_{\mathrm{c}}. \tag{8}$$

The $K_{\mathrm{c(sep)}}$ can be estimated by using a theoretical equation for ion association,[1,7,8] since the formation of a solvent-separated ion pair is presumed to be governed by such a simple electrostatic interaction as that explained by theory. The inter-ionic distance for a solvent-separated ion pair, which is included in the theoretical equation, was taken as being the sum of $\sum r_{\mathrm{ef}}$ and $2r(\mathrm{H_2O})$, where $2r(\mathrm{H_2O})$ is the diameter of a water molecule and was regarded as being 0.28 nm; $\sum r_{\mathrm{ef}}$ is the sum of the effective ionic radii of the cation and the anion, the values of which were regarded as being 0.362 nm for $[\mathrm{Cr(en)_3}]^{3+}$, 0.445 nm for *lel*$_3$-$[\mathrm{Cr(chxn)_3}]^{3+}$ (*lel*$_3$=*lel*,*lel*,*lel*), 0.498 nm for $[\mathrm{Cr(phen)_3}]^{3+}$, 0.257 nm for $\mathrm{CH_3SO_3^-}$, and 0.315 nm for $(\mathrm{CH_2SO_3})_2{}^{2-}$.[1] The values of $x_{\mathrm{MA(con)}}$, $\sum r_{\mathrm{ef}}$, and $K_{\mathrm{c(sep)}}$ are summarized in Table 1 and those of $(\Delta\nu_{1/2})_{\mathrm{MA(con)}}$ obtained are shown in Table 2.

The theoretical expression for $(\Delta\nu_{1/2})_{\mathrm{MA(con)}}$ is given by Eq. 1, where $(\Delta\nu_{1/2})_{\mathrm{IP}}$ should be replaced by $(\Delta\nu_{1/2})_{\mathrm{MA(con)}}$ and the second term in the brackets can be neglected since $\omega_{\mathrm{S}}{}^2\tau_{\mathrm{C}}{}^2 \gg 1$, where $\omega_{\mathrm{S}}$ is $1.12\times10^{12}\,\mathrm{s^{-1}}$ and $\tau_{\mathrm{C}}$ is larger than $10^{-11}$ s; the latter condition is demonstrated below. If we assume that the sulfonate anion is tightly bound to the complex ion in the ion pair and that the two ions rotate together, by keeping their configurations we can express the dipolar correlation time ($\tau_{\mathrm{C}}$) by

$$\tau_{\mathrm{C}}{}^{-1} = \tau_{\mathrm{R}}{}^{-1} + \tau_{\mathrm{MA(con)}}{}^{-1} + \tau_{\mathrm{S}}{}^{-1}, \tag{9}$$

where $\tau_{\mathrm{R}}$ and $\tau_{\mathrm{MA(con)}}$ are the rotational correlation time and the lifetime of the contact ion pair, respectively, and $\tau_{\mathrm{S}}$ is the electron spin-lattice relaxation time. In the present systems, the contributions of $\tau_{\mathrm{MA(con)}}{}^{-1}$ and $\tau_{\mathrm{S}}{}^{-1}$ to $\tau_{\mathrm{C}}{}^{-1}$ were neglected, since these are relatively small compared with that of $\tau_{\mathrm{R}}{}^{-1}$, as described later. A value of $5\times10^{-9}$ s has been reported for $\tau_{\mathrm{MA(con)}}$ for the

Table 1. Values of $\sum r_{\mathrm{ef}}$, $\log K_{\mathrm{c}}$, $\log K_{\mathrm{c(sep)}}$, and $x_{\mathrm{MA(con)}}$ for Each Ion Pair

| Ion pair | $\sum r_{\mathrm{ef}}$/nm | $\log K_{\mathrm{c}}$[a] | $\log K_{\mathrm{c(sep)}}$[c] | $x_{\mathrm{MA(con)}}$ |
|---|---|---|---|---|
| $[\mathrm{Cr(en)_3}]^{3+}\mathrm{CH_3SO_3^-}$ | 0.619 | 1.26±0.05 | 0.95 | 0.51±0.06 |
| $[\mathrm{Cr(en)_3}]^{3+}(\mathrm{CH_2SO_3})_2{}^{2-}$ | 0.677 | 2.35±0.02 | 1.96 | 0.60±0.03 |
| *lel*$_3$-$[\mathrm{Cr(chxn)_3}]^{3+}\mathrm{CH_3SO_3^-}$ | 0.702 | 1.26±0.05 | 0.91 | 0.55±0.05 |
| *lel*$_3$-$[\mathrm{Cr(chxn)_3}]^{3+}(\mathrm{CH_2SO_3})_2{}^{2-}$ | 0.760 | 2.43±0.01 | 1.91 | 0.70±0.01 |
| $[\mathrm{Cr(phen)_3}]^{3+}\mathrm{CH_3SO_3^-}$ | 0.755 | 1.04[b] | 0.89 | 0.3 |
| $[\mathrm{Cr(phen)_3}]^{3+}(\mathrm{CH_2SO_3})_2{}^{2-}$ | 0.813 | 2.13±0.01 | 1.89 | 0.42±0.02 |

a) Experimental values at $I$=0.01 (25 °C).[1] b) Theoretical value at $I$=0.01 where the inter-ionic distance used in the calculation is the sum of the effective ionic radii of the cation and the anion (25 °C).[1,8] c) Theoretical values at $I$=0.01 (25 °C).[8]

Table 2. Values of $(\Delta\nu_{1/2})_{\mathrm{obsd}}$, $P_{\mathrm{A}}$, and $x_{\mathrm{MA(con)}}(\Delta\nu_{1/2})_{\mathrm{MA(con)}}$

(1) $CH_3SO_3^-$

| Complex | $c$(complex) | $(\Delta\nu_{1/2})_{\mathrm{obsd}}$ | $P_{\mathrm{A}}$ | $x_{\mathrm{MA(con)}}(\Delta\nu_{1/2})_{\mathrm{MA(con)}}$ |
|---|---|---|---|---|
| | $10^{-2}$ mol dm$^{-3}$ | Hz | | Hz |
| $[Cr(en)_3]^{3+}$ | 0.600 | 7.5 | 0.942 | 129 |
| | 0.800 | 9.1 | 0.929 | 128 |
| | 1.00 | 11.2 | 0.918 | 137 |
| | 1.50 | 14.7 | 0.895 | 140 |
| | 2.00 | 16.8 | 0.876 | 135 |
| *lel*$_3$-$[Cr(chxn)_3]^{3+}$ | 0.600 | 16.5 | 0.940 | 277 |
| | 0.800 | 20.3 | 0.927 | 279 |
| | 1.00 | 24.6 | 0.915 | 290 |
| | 1.50 | 33.5 | 0.890 | 305 |
| | 2.00 | 39.6 | 0.869 | 302 |
| $[Cr(phen)_3]^{3+}$ | 0.600 | 5.7 | 0.961 | 147 |
| | 0.800 | 6.8 | 0.952 | 143 |
| | 1.00 | 8.5 | 0.944 | 153 |
| | 1.50 | 11.4 | 0.927 | 156 |
| | 2.00 | 13.3 | 0.912 | 151 |

(2) $(CH_2SO_3)_2^{2-}$

| Complex | $c$(complex) | $(\Delta\nu_{1/2})_{\mathrm{obsd}}$ | $P_{\mathrm{A}}$ | $x_{\mathrm{MA(con)}}(\Delta\nu_{1/2})_{\mathrm{MA(con)}}$ |
|---|---|---|---|---|
| | $10^{-2}$ mol dm$^{-3}$ | Hz | | Hz |
| $[Cr(en)_3]^{3+}$ | 0.600 | 35.6 | 0.786 | 166 |
| | 0.800 | 48.4 | 0.746 | 191 |
| | 1.00 | 55.7 | 0.714 | 195 |
| | 1.50 | 74.9 | 0.658 | 219 |
| | 2.00 | 79.0 | 0.621 | 208 |
| *lel*$_3$-$[Cr(chxn)_3]^{3+}$ | 0.600 | 88.9 | 0.755 | 363 |
| | 0.800 | 110.5 | 0.707 | 377 |
| | 1.00 | 122.8 | 0.669 | 371 |
| | 1.50 | 150.4 | 0.600 | 376 |
| | 2.00 | 170.0 | 0.555 | 382 |
| $[Cr(phen)_3]^{3+}$ | 0.600 | 34.3 | 0.830 | 202 |
| | 0.800 | 41.5 | 0.796 | 203 |
| | 1.00 | 48.8 | 0.769 | 211 |
| | 1.50 | 57.6 | 0.717 | 204 |
| | 2.00 | 67.0 | 0.680 | 209 |

ion pair $[Co(en)_3]^{3+}SO_4^{2-}$ from an ultrasonic absorption measurement;[9] the value of $\tau_{\mathrm{S}}$ for the aqua chromium(III) complex is around $5\times10^{-10}$ s,[10] although those for the chromium(III) complexes used here are not available (we assume that the $\tau_{\mathrm{S}}$ values are close to that for the aqua complex). On the other hand, the values of $\tau_{\mathrm{R}}$ for the ion pairs of $[Co(en)_3]^{3+}$ with some monovalent and divalent anions are 3.2 to $8.7\times10^{-11}$ s at 33 °C; that for the ion pair of $[Co(phen)_3]^{3+}$ with a sulfate ion is $1.2\times10^{-10}$ s at the same temperature.[2]

The values of $\tau_{\mathrm{R}}$ for unpaired $[Co(en)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ are $3.2\times10^{-11}$ and $1.0\times10^{-10}$ s at 33 °C, respectively, and are well represented by assuming nearly sticking hydrodynamic boundary conditions on the Stokes–Einstein–Debye relation:[2]

$$\tau_{\mathrm{R}} = CV_{\mathrm{R}}\eta/kT, \tag{10}$$

where $V_{\mathrm{R}}$ is the volume of rotating molecule, $\eta$ the viscosity of the solution, and $C$ a dimensionless parameter related to the shape of the rotating molecule and the hydrodynamic boundary condition. We used this equation in order to estimate the possible range of $\tau_{\mathrm{R}}$ by assuming a sticking boundary condition with the following two extreme cases: In case 1, the ion pair could be regarded as being a sphere having a volume equal to the sum of the van der Waals' volumes of the cation and the anion; this corresponds to the assumption that $V_{\mathrm{R}}=\sum 4\pi r_{\mathrm{ef}}^3/3$ and $C=1$ and gives the smallest $\tau_{\mathrm{R}}$. In case 2, the ion pair could be regarded as being a rotational ellipsoid of prolate shape having major and minor axes lengths of $2a=2\sum r_{\mathrm{ef}}$ and $2b=2r_{\mathrm{ef(complex)}}$, respectively, and a volume of $V_{\mathrm{R}}=4\pi ab^2/3$. The rotation of the major axis gives the largest $\tau_{\mathrm{R}}$, where $C$ can be calculated as a function of the ratio $a/b$ from the relation $(\xi^*/8)\cdot(a/b)^2$, where $\xi^*$ is a dimensionless friction coefficient defined by Hu and Zwanzig;[11] its values for the sticking boundary condition have been given.[11,12] The values of $V_{\mathrm{R}}$ in both cases and those of $C$ in Case 2 are shown in Table 3.

Table 3. Values of $(\Delta\nu_{1/2})_{\mathrm{MA(con)}}$, $\tau_{\mathrm{R}}/r_{\mathrm{CrH}}^6$, $C$, $V_{\mathrm{R}}$, and $r_{\mathrm{CrH}}$ for Each Ion Pair

| Ion pair | $(\Delta\nu_{1/2})_{\mathrm{MA(con)}}$[a] | $\tau_{\mathrm{R}}/r_{\mathrm{CrH}}^6$ | Case 1[b] | | Case 2[b] | | |
|---|---|---|---|---|---|---|---|
| | Hz | $10^{-9}$ s nm$^{-6}$ | $V_{\mathrm{R}}$ nm$^3$ | $r_{\mathrm{CrH}}$ nm | $C$ | $V_{\mathrm{R}}$ nm$^3$ | $r_{\mathrm{CrH}}$ nm |
| $[\mathrm{Cr(en)_3}]^{3+}\mathrm{CH_3SO_3}^-$ | 260±40 | 1.90±0.30 | 0.270 | 0.56±0.02 | 1.31 | 0.340 | 0.60±0.02 |
| $[\mathrm{Cr(en)_3}]^{3+}(\mathrm{CH_2SO_3})_2{}^{2-}$ | 320±50 | 2.34±0.37 | 0.330 | 0.56±0.02 | 1.42 | 0.372 | 0.60±0.02 |
| *lel*$_3$-$[\mathrm{Cr(chxn)_3}]^{3+}\mathrm{CH_3SO_3}^-$ | 520±60 | 3.80±0.44 | 0.440 | 0.54±0.02 | 1.24 | 0.582 | 0.58±0.02 |
| *lel*$_3$-$[\mathrm{Cr(chxn)_3}]^{3+}(\mathrm{CH_2SO_3})_2{}^{2-}$ | 520±20 | 3.80±0.15 | 0.500 | 0.55±0.01 | 1.31 | 0.630 | 0.60±0.01 |
| $[\mathrm{Cr(phen)_3}]^{3+}\mathrm{CH_3SO_3}^-$ | 490±60 | 3.58±0.44 | 0.588 | 0.57±0.02 | 1.21 | 0.784 | 0.62±0.02 |
| $[\mathrm{Cr(phen)_3}]^{3+}(\mathrm{CH_2SO_3})_2{}^{2-}$ | 470±30 | 3.43±0.22 | 0.648 | 0.58±0.01 | 1.27 | 0.845 | 0.63±0.01 |

a) After the viscosity correction. b) See text.

From Eqs. 1, 9, and 10 and the above-mentioned considerations,

$$(\Delta\nu_{1/2})_{\mathrm{MA(con)}} = (7J/15\pi)\tau_{\mathrm{R}}/r_{\mathrm{CrH}}^6 = (7J\eta/15\pi kT)(CV_{\mathrm{R}}/r_{\mathrm{CrH}}^6). \quad (11)$$

Here, $J$ is $9.2\times10^{-43}$ s$^{-2}$ m$^6$, which was obtained from Eq. 2 by taking $S=3/2$, $\gamma_{\mathrm{H}}=2.675\times10^8$ s$^{-1}$ T$^{-1}$, $g=2.00$, and $\beta=9.27\times10^{-24}$ JT$^{-1}$.[5] The viscosities of solutions, $\eta$, in Eq. 11 were estimated by using the following approximated expression for the Jones-Dole's equation[13] on a mixed electrolyte solution:

$$\eta = \eta_0(1 + \textstyle\sum B_i c_i), \quad (12)$$

where $\eta_0$ is the viscosity of water at 27 °C (being equal to $8.51\times10^{-4}$ Pa s[14]) $c_i$ is the salt concentration, and $B_i$ is the so-called $B$ coefficient of the salt; the $A\sqrt{c_i}$ term in the Jones-Dole equation was ignored. The following values of $B$ in dm$^3$ mol$^{-1}$ at 25 °C were used for the present calculations: 0.198 for $\mathrm{CH_3SO_3Na}$,[15] 0.403 for $(\mathrm{CH_2SO_3Na})_2$,[16] 0.53 for $[\mathrm{Cr(en)_3}]\mathrm{Cl_3}$,[17] and 1.52 for $[\mathrm{Cr(phen)_3}]\mathrm{Cl_3}$ and *lel*$_3$-$[\mathrm{Cr(chxn)_3}]\mathrm{Cl_3}$.[18] The difference between $\eta$ and $\eta_0$ were within 3% under the present conditions and led to only small differences within 10 Hz in $(\Delta\nu_{1/2})_{\mathrm{MA(con)}}$. The averaged values of $(\Delta\nu_{1/2})_{\mathrm{MA(con)}}$ after the viscosity correction were used for the calculation of $\tau_{\mathrm{R}}/r_{\mathrm{CrH}}^6$ by the use of Eq. 11.

The values of $(\Delta\nu_{1/2})_{\mathrm{MA(con)}}$ and $\tau_{\mathrm{R}}/r_{\mathrm{CrH}}^6$ and the resulting ones of $r_{\mathrm{CrH}}$ estimated for Case 1 and Case 2 are summarized in Table 3. The differences in $r_{\mathrm{CrH}}$ between the two cases were about 0.04—0.05 nm. When $r_{\mathrm{CrH}}$ is compared with $\sum r_{\mathrm{ef}}$ in Case 1 or Case 2, we can say follows: the differences in $r_{\mathrm{CrH}}$ between the contact ion pairs of $\mathrm{CH_3SO_3}^-$ and $(\mathrm{CH_2SO_3})_2{}^{2-}$ for the same complex are very small, in spite of the fact that the anions have a difference of $5.8\times10^{-2}$ nm with $\sum r_{\mathrm{ef}}$; the differences in $r_{\mathrm{CrH}}$ between different complexes for the same anion are also significantly smaller than those in $\sum r_{\mathrm{ef}}$; the absolute values of $r_{\mathrm{CrH}}$ are smaller than those of $\sum r_{\mathrm{ef}}$. It should be noted that $\sum r_{\mathrm{ef}}$ corresponds to a kind of averaged contact distance between the center of the complex ion and that of the anion, since the $r_{\mathrm{ef}}$ values of the ions were derived from their van der Waals' volumes by regarding them as spherical.[1] The complex ions, *lel*$_3$-$[\mathrm{Cr(chxn)_3}]^{3+}$ and $[\mathrm{Cr(phen)_3}]^{3+}$, have open spaces along the $C_3$-axis and hollows between the ligands, which can receive an anion. When an anion comes into contact with a complex in such a location, their contact distance becomes shorter than $\sum r_{\mathrm{ef}}$. However, the distance between the Cr(III) atom of the complex and the H atoms of the anion ($r_{\mathrm{CrH}}$) depends on the stereochemical configuration of the contact ion pair.

The values of $r_{\mathrm{CrH}}$ obtained for the ion pairs of $\mathrm{CH_3SO_3}^-$ are in a range 0.54 to 0.62 nm (Table 3), in agreement with the configuration of the ion pair that the sulfonate group of the anion is directed toward the Cr(III) atom in the open spaces along the $C_3$-axis of the complex or in the hollows between the ligands: the Cr–H distances presumed for such configurations from the Stuart-type molecular models are around 0.6 nm for the ion pair of $[\mathrm{Cr(en)_3}]^{3+}$ or $[\mathrm{Cr(chxn)_3}]^{3+}$ and about 0.6—0.7 nm for that of $[\mathrm{Cr(phen)_3}]^{3+}$; if the methyl group of $\mathrm{CH_3SO_3}^-$ is directed toward the Cr(III) atom in the same positions around the complex (as stated above), the Cr–H distances are presumed to be around 0.35 nm for an ion pair of $[\mathrm{Cr(en)_3}]^{3+}$ or $[\mathrm{Cr(chxn)_3}]^{3+}$ and around 0.4 nm for that of $[\mathrm{Cr(phen)_3}]^{3+}$. For the last two ion pairs, however, we cannot completely exclude the configuration that the methyl group is directed to the Cr(III) atom across one chxn or phen ligand, since it gives about 0.5—0.7 nm for the Cr(III)–H distance.

The $(\mathrm{CH_2SO_3})_2{}^{2-}$ ion could stereochemically have two types of conformations (trans and gauche forms) with the two sulfonate groups. The values of $r_{\mathrm{CrH}}$ obtained for the ion pairs of $(\mathrm{CH_2SO_3})_2{}^{2-}$ are in the range 0.55 to 0.63 nm, suggesting the following probable configurations of the contact ion pairs: when the conformation is gauche, one or two sulfonate groups are directed toward the Cr(III) atom in the space along the $C_3$-axis or in the hollows between the ligands; when the conformation is trans, one sulfonate group is directed toward the Cr(III) atom in the same positions. However, we could not decide which conformation of the $(\mathrm{CH_2SO_3})_2{}^{2-}$ ion is dominant in the contact ion pairs. The Cr(III)–H distances presumed from the molecular models are as follows: in the case of the gauche form of the anion, it is about 0.5—0.7 nm for the ion pairs of $[Cr(en)_3]^{3+}$ or $[Cr(chxn)_3]^{3+}$ and about 0.6—0.8 nm for that of $[Cr(phen)_3]^{3+}$; in the case of the trans form, similar distances are estimated for the ion pairs of $CH_3SO_3^-$. The possibility of other configurations is similar, as described for the ion pairs of $CH_3SO_3^-$.

The results obtained for $r_{CrH}$ are consistent with the predictions from the molecular models (as described above). This suggests that the several assumptions made in the present study are reasonable, especially that the lifetimes of detected contact ion pairs having a given configuration are longer than $\tau_R$. Such tight configurations may be maintained by the short-range interactions between the sulfonate group of the anions and the amino groups of $[Cr(en)_3]^{3+}$ or $[Cr(chxn)_3]^{3+}$, and also by a partial separation of anions from the atmosphere of the solvent into the hollows of the complex.

The values of $\log K_c$ or $\log K_{c(con)}$ for ion-pair formation of *lel*$_3$-$[Cr(chxn)_3]^{3+}$ with anions are similar to or slightly larger than those of $[Cr(en)_3]^{3+}$, in spite of the former complex ion having a relatively large ionic size. This may be due to the difference in the hydration of the complex ions and/or to the presence of some specific interactions, such as a hydrophobic type, due to the chxn ligand in the formation of *lel*$_3$-$[Cr(chxn)_3]^{3+}(CH_2SO_3)_2^{2-}$. In either case, not only the positively charged sites, such as the hydrogen atoms of the amino group in the ligand, but also the hollows among the ligands which can receive the anion may contribute to the formation of a contact ion pair. These considerations are supported by the $r_{CrH}$ values obtained in the present study, which give the information concerning the major position of the hydrogen atoms of the anion around the complex ion in the contact ion pair.

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