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Kinetic Study of the Hydrolysis of Sulfamido, *p*-Toluenesulfonamido, and *p*-Nitrobenzenesulfonamido Complexes of Pentaamminecobalt(III) in Acidic Aqueous Solution

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The pentaamminecobalt(III) complexes of $NH_2SO_2NH^-$, p-$CH_3C_6H_4SO_2NH^-$, and p-$NO_2C_6H_4SO_2NH^-$ have been prepared and characterized. The rate law for the hydrolysis of $(NH_3)_5CoNHSO_2NH_2^{2+}$ has the form $-d\ln[complex]/dt = k_2[H^+]/(K_a + [H^+])$. The rate constant and acid dissociation constant (25 °C, μ = 1.0 M $LiClO/HClO_4$), with their corresponding enthalpies and entropies, are as follows: $k_2 = 1.41 \times 10^{-2}$ s^{-1}, $\Delta H^\ddagger = 21.7$ kcal mol^{-1}, $\Delta S^\ddagger = 5.5$ cal mol^{-1} deg^{-1}; $K_a = 0.58$ M, $\Delta H^\circ = 2.7$ kcal mol^{-1}, $\Delta S^\circ = 7.9$ cal mol^{-1} deg^{-1}. The hydrolysis kinetics of the aromatic sulfonamido complexes are consistent with the same rate law if $K_a \gg [H^+]$. The rate constants (25 °C, μ = 1.0 M $LiClO_4/HClO_4$), activation enthalpy and entropy for p-CH_3 and p-NO_2, respectively, are as follows: $k_2/K_a = 2.15 \times 10^{-2}$ M^{-1} s^{-1}, $\Delta H^\ddagger = 19.0$ kcal mol^{-1}, $\Delta S^\ddagger = -2.5$ cal mol^{-1} deg^{-1}; $k_2/K_a = 5.71 \times 10^{-3}$ M^{-1} s$^-$ s^{-1}, $\Delta H^\ddagger = 18.0$ kcal mol^{-1}, $\Delta S^\ddagger = -8.4$ cal mol^{-1} deg^{-1}. The unusually large aquation rate constants are attributed to N-protonation of (NH_3) $CoNHSO_2^{2+}$ followed by facile release of the neutral ligand.

Introduction

Aromatic sulfonamides are well-known to be strong inhibitors of carbonic anhydrase. These systems have been studied by a wide range of techniques[1-7] with general agreement that the sulfonamide is complexed as the anion to zinc(II), or to cobalt(II) in the modified enzyme. Kinetic studies are consistent with a complex formation mechanism involving preassociation of sulfonamide and the enzyme followed by rate-controlling metal–sulfonamide bond formation.[1] However, the sequence of proton transfer steps remains in doubt.

Despite the considerable biochemical work on sulfonamide complexes, there have been very few simple inorganic sulfonamide complexes prepared. Traube[8,9] first prepared silver(I) complexes of sulfamide. The structure of $Ag_2(N_2H_2SO_2)$ recently has been shown[10] to have two nitrogen atoms from different $N_2H_2SO_2^{2-}$ ions coordinated to silver(I). Ouchi and Moeller[11] prepared some $M(en)_2$–sulfamide derivatives ($M = Cu^{2+}$, Ni^{2+}), which are the subject of a recent infrared study.[12] Beck and Cenini and co-workers[13-15] have prepared aromatic sulfonamide derivatives such as $((C_2H_5)_3P)_2(Cl)Pt(NHSO_2C_6H_5)$ and $(bpy)Pd(NHSO_3C_6H_4CH_3)_2$ by reactions of sulfonyl azides.

Mann[16] prepared and resolved *cis*-$[Rh(N_2H_2SO_2)_2(OH_2)_2]^-$. This seems to have been the second example of a purely inorganic optically active species. Mann also prepared $[Pt(OH)(NH_3)(N_2H_2SO_2)_2]^-$ and noted that the rhodium(III) and especially the platinum(IV) complexes are very susceptible to decomposition by even very weak acids used as resolving agents.

In the present study the pentaamminecobalt(III) complexes of sulfamide, *p*-toluenesulfonamide, and *p*-nitrobenzenesulfonamide have been prepared and characterized. The acid–base properties and hydrolysis kinetics have been investigated. The results have been related to previous studies on cobalt(III) complexes and to the properties of the sulfonamide–carbonic anhydrase complexes.

Experimental Section

Reagents. All solutions were prepared in water redistilled from alkaline permanganate in an all-glass apparatus. Lithium perchlorate was prepared and standardized as described previously.[17]

Preparation of $[(NH_3)_5CoNHSO_2NH_2]BrClO_4$. A solution containing 5 g of sulfamide and 1 mL of 2,6-lutidine in 40 mL of acetone was allowed to stand over molecular sieves for 1 h, and then 4 g of $((NH_3)_5CoO_3SCF_3)(O_3SCF_3)_2$ was added. After 14 h the mixture was filtered to remove the molecular sieves, and 3 g of LiBr was added. The product was collected, washed with acetone, redissolved in a minimum of warm (50 °C) water, and precipitated by addition of $NaClO_4$ and cooling. This product was collected and recrystallized from a minimum of warm water to yield dark red crystals, which were washed with methanol and air-dried.

Anal. Calcd for $[(NH_3)_5CoNHSO_2NH_2]BrClO_4$: N, 23.43; H, 4.33. Found: N, 23.44; H, 4.36.

The electronic spectrum in water has a peak at 501 nm (ϵ 78 cm^{-1} M^{-1}), a shoulder at 350 nm (ϵ 119 cm^{-1} M^{-1}), and a shoulder at 270 nm (e 1.38×10^3 cm^{-1} M^{-1}). The ^{1}H NMR spectrum shows peaks for cis NH_3 (τ 6.70), trans NH_3 (τ 6.88), sulfamido NH (τ 8.38), and sulfamido NH_2 (τ 4.24) relative to Me_2SO-d_6 (τ 7.50). The infrared spectrum of the dibromide salt was analyzed by comparison to the spectra of the free ligand[18] and the dibromide salt of the deuterated complex. Characteristic ligand vibrations in the complex are SO_2 stretch at 1224 cm^{-1} (antisym) and 1132 cm^{-1} (sym) and N–S stretch at 993 cm^{-1}, while for the deuterated complex the corresponding vibrations are at 1275, 1126, and 989 cm^{-1}, respectively. In the free ligand these vibrations are observed at 1358, 1156, and 904 cm^{-1}, respectively.

Preparation of $[(NH_3)_5CoNHSO_2C_6H_4CH_3](ClO_4)_2$. A solution of aquopentaamminecobalt(III) perchlorate (13.5 g) in dry *N*,*N*-dimethylacetamide (40 mL) over molecular sieves (10 g) was heated on a steam bath for 1 h. The *p*-toluenesulfonamide (10 g) was dissolved in dry *N*,*N*-dimethylacetamide (20 mL) containing 3.4 mL of 2,6-lutidine and molecular sieves (10 g) and heated on a steam bath for 1 h. The two solutions were mixed, heated on a steam bath for 6 h, cooled, filtered, and dripped into a 50:50 mixture of ether and 2-butanol. The crude product was collected, redissolved in water (500 mL), and purified by cation-exchange chromatography on Baker CGC-271 weak-acid resin (J. T. Baker Chemical Co.) in the sodium

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ion form (1 in. × 5.5 in.). Elution with increasing concentrations of sodium perchlorate up to 0.2 M separated the complex from impurities remaining at the top of the column. The resin containing the desired complex was separated physically and washed with distilled water followed by acetic acid (4 M) in order to remove the complex from the resin. The resulting solution was neutralized with sodium hydroxide and the complex precipitated with $NaClO_4$. The complex was recrystallized from water, washed with ether, and air-dried to yield a purple crystalline solid.

Anal. Calcd for $[(NH_3)_5CoNHSO_2C_6H_4CH_3](ClO_4)_2 \cdot H_2O$: N, 15.82; C, 15.83; H, 4.74. Found: N, 15.91; C, 15.92; H, 4.75.

The electronic spectrum in water shows a peak at 505 nm (ϵ 88 cm^{-1} M^{-1}) and a shoulder at 290 nm (ϵ 1.74 × 10^3 cm^{-1} M^{-1}). The ^1H NMR spectrum has peaks for cis NH_3 (τ 6.67), trans NH_3 (τ 6.97), sulfonamido NH (τ 7.97), toluene CH_3 (τ 7.64), C_6H_4 (τ 2.27, 2.36, 2.62, 2.72), and H_2O (τ 6.70) relative to Me_2SO-d_6 (τ 7.50). The infrared spectrum has analyzed by comparison to the spectra of the free ligand, the deuterated complex, and various sulfonamide derivatives of platinum and palladium complexes.[13-15] The characteristic ligand vibrations in the complex are SO_2 stretch at 1214 cm^{-1} (antisym) and 1122 cm^{-1} (sym) and N–S stretch at 963 cm^{-1}, while in the deuterated complex the corresponding vibrations are at 1238, 1122, and 1010 cm^{-1}, respectively. In the free ligand these vibrations are observed at 1323, 1170, and 909 cm^{-1}, respectively.

Preparation of $[(NH_3)_5CoNHSO_2C_6H_4NO_2](ClO_4)_2$. A solution of aquopentaamminecobalt(III) perchlorate (5.7 g) in dry *N,N*-dimethylacetamide (20 mL) with molecular sieves (10 g) was heated on a steam bath for 2 h. The *p*-nitrobenzenesulfonamide (5 g) was dissolved in a minimum amount of hot, dry *N,N*-dimethylacetamide to which 3 mL of 2,6-lutidine and molecular sieves (10 g) had been added. The two solutions were mixed, heated for 3 h on a steam bath, cooled, and filtered, and the solvent was extracted with ether. The resulting oil was dissolved in a minimum amount of warm water and the complex precipitated by the addition of sodium perchlorate. The crude product was collected, redissolved in 250 mL of 0.02 M $NaClO_4$, purified by ion-exchange chromatography, and recrystallized as described for the *p*-toluenesulfonamide complex.

Anal. Calcd for $[(NH_3)_5CoNHSO_2C_6H_4NO_2](ClO_4)_2 \cdot H_2O$: N, 17.44; C, 12.82; H, 3.94. Found: N, 17.42; C, 12.62; H, 3.66.

The electronic spectrum in water shows peaks at 501 nm (ϵ 86 cm^{-1} M^{-1}) and 260 nm (ϵ 9.75 × 10^3 cm^{-1} M^{-1}). The ^1H NMR spectrum has peaks for cis NH_3 (τ 6.66), trans NH_3 (τ 6.96), C_6H_4 (τ 1.58, 1.68, 1.96, 2.06), and H_2O (τ 6.70) relative to Me_2SO-d_6 (τ 7.50). The sulfonamido NH peak was not observed. The infrared spectrum was analyzed by comparison to the spectra of the free ligand and the *p*-toluene- and deuterated *p*-toluenesulfonamido complexes discussed above. The characteristic ligand vibrations in the complex are SO_2 stretch at 1241 cm^{-1} (antisym) and 1140 cm^{-1} (sym), N–S stretch at 988 cm^{-1}, and NO_2 stretch at 1524 cm^{-1} (antisym) and 1354 cm^{-1} (sym). In the free ligand these vibrations are observed at 1315, 1165, 901, 1521, and 1351 cm^{-1}, respectively.

Kinetic Measurements. The hydrolysis of the sulfamido complex was studied by injecting an aqueous solution of the cobalt(III) complex into a temperature-equilibrated aqueous perchloric acid solution containing the required amount of lithium perchlorate. The hydrolyses of the *p*-toluenesulfonamido and *p*-nitrobenzenesulfonamido complexes were studied similarly except that the perchloric acid was the last component to be injected. The kinetics were followed at 285 and 295 nm on a Cary 219 spectrophotometer and at 290 nm on a Baush and Lomb Precision spectrophotometer for the sulfamido, *p*-nitrobenzenesulfonamido, and *p*-toluenesulfonamido complexes, respectively. All systems were studied under pseudo-first-order conditions with perchloric acid in more than 20-fold excess over cobalt(III).

The rate constants were determined from the usual semilogarithmic plots of absorbance change vs. time. The plots were linear for at least 90% of the reaction. The temperature was controlled by a water circulation system described elsewhere,[17] and the temperature inside the cell was checked periodically with a thermocouple.

Reaction Product Analysis. The reaction solution for the *p*-toluenesulfonamido complex typically contained 20 mg of the cobalt(III) complex and 0.10 or 0.80 M perchloric acid in a total volume of ~15 mL adjusted to a total ionic strength of 1.0 M with lithium perchlorate. The hydrolysis was allowed to proceed for 10 half-times, and then the solution was neutralized with 5 M NaOH, diluted to a total volume of ~125 mL, and charged onto a $^1/_2$ in. × $^1/_2$ in. cation-exchange column of Baker CGC-271 weak-acid resin in the sodium ion form. The initial eluate was collected, acidified to pH ~5, and analyzed spectrophotometrically for *p*-toluenesulfonamide (ϵ 528 cm^{-1} M^{-1} at 262 nm, pH <7). The electronic spectrum of the latter easily distinguishes it from *p*-toluenesulfonic acid. The resin containing the cobalt(III) product was separated physically and washed with water followed by 4 M $HClO_4$ in order to remove the cobalt(III) complex. The resulting solution was diluted to 1.0 M $HClO_4$ and analyzed spectrophotometrically for $(NH_3)_5CoOH_2^{3+}$ (ϵ 46 cm^{-1} M^{-1} at 345 nm; ϵ 49 cm^{-1} M^{-1} at 492 nm).

A second column was charged with a blank solution containing no cobalt(III). The respective eluates obtained from the identical workup of this column were used as blanks in the spectrophotometric analysis of both products.

The reaction solution for the *p*-nitrobenzenesulfonamido complex contained 6–14 mg of the cobalt(III) complex and 0.10 or 1.00 M $HClO_4$ in a total volume of ~10 mL (μ = 1.0 M). The products were analyzed as described above except that the initial eluate was made 1.0 M in NaOH and analyzed spectrophotometrically for $NHSO_2C_6H_4NO_2^-$ (ϵ 8.66 × 10^3 cm^{-1} M^{-1} at 276 nm), allowing distinction between the amide and *p*-nitrobenzenesulfonic acid.

The reaction solution for the sulfamido complex contained ~15 mg of the cobalt(III) complex and 0.05 or 1.0 M $HClO_4$ in a total volume of ~6 mL (μ = 1.0 M). Analysis of the products was carried out as described above except that the initial eluate was not analyzed for free ligand because sulfamide has no characteristic absorbance in the UV–visible spectrum.

Physical Measurements. Electronic spectra were recorded on a Unicam SP1700 or a Cary 219 spectrophotometer. The ^1H NMR spectra were obtained in deuterated dimethyl sulfoxide on a Varian A56/60 or a Perkin-Elmer R32 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 421 grating or a Nicolet-FT-7000 spectrometer in KBr pellets.

Results and Discussion

The sulfamide and sulfonamide ligands may coordinate to cobalt(III) through the nitrogen or oxygen atoms. Previous work[13-16] with other metal ions indicates that N-coordination is at least possible, if not preferred. The fact that the ligands coordinate as the anion seems more consistent with N-coordination. The observation[19] that sulfamate is nitrogen bonded to $(NH_3)_5Co^{3+}$ also leads one to expect N-coordination for sulfamide and the sulfonamides.

The properties of the complexes are most consistent with N-coordination. Thus, the chemical shift difference between the cis and trans NH_3 protons of 0.18, 0.30, and 0.30 τ unit for the sulfamide, *p*-toluenesulfonamide, and *p*-nitrobenzenesulfonamide, respectively, are typical of N-bonded ligands (0–0.6 τ unit) compared to O-bonded ligands (1.0–1.5 τ units).[17,20] The infrared spectra are consistent with previously proposed N-bonded complexes[13-15] but are not very diagnostic in the absence of O-bonded models.

Kinetic and spectrophotometric observations discussed below indicate that these complexes can be protonated, and the protonated complex of sulfamide has a K_a = 0.55 M, while the values for the aromatic sulfonamides are >5 M. Therefore, coordination to $(NH_3)_5Co^{3+}$ has increased the K_a of the ligands by about a factor of 10^{10} compared to that of the free ligand.[1,2] Analogous large changes are noted for other systems in which the atom coordinated to cobalt(III) also carried an ionizable hydrogen such as water,[21] sulfamate,[19] and N-bonded formamide.[20] Conversely, if the ionizable hydrogen is not on the coordinated atom, much smaller changes in K_a are observed, as for example in the case of carbonate[22] and phosphate.[23] As a result of these observations the subsequent discussion will consider all three ligands to be N-bonded to cobalt(III).

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Table I. Hydrolysis Kinetic Data for $(NH_3)_5CoNHSO_2NH_2^{2+}$ in 1.0 M $LiClO_4$-$HClO_4$[a]

temp, °C	[H⁺], M	10^3k_{obsd}, s^{-1} obsd[b]	calcd[c]
15.0	0.0200	0.148	0.144
15.0	0.0250	0.180	0.178
15.0	0.0400	0.271	0.276
15.0	0.0999	0.599	0.617
15.0	0.999	2.40	2.38
25.1	0.0200	0.468	0.470
25.0	0.0250	0.592	0.583
25.0	0.0400	0.908	0.909
25.0	0.0999	2.05	2.07
25.1	0.999	8.95	8.93
34.9	0.0200	1.35	1.33
34.9	0.0333	2.14	2.17
34.9	0.0999	6.02	5.92
34.9	0.200	10.3	10.4
34.9	0.400	16.8	16.9
34.9	0.799	24.7	24.5
34.9	0.999	26.9	26.9

[a] The cobalt(III) concentration was (1.3–2.5) × 10^{-4} M. [b] Values are the average of at least two runs. [c] Calculated from eq 1 with 10^2a = 0.35 ± 0.03, 1.41 ± 0.06, and 4.42 ± 0.20 s^{-1} and b = 0.47 ± 0.04, 0.58 ± 0.03, and 0.65 ± 0.04 M at 15.0, 25.0, and 34.9 °C, respectively. Errors are 95% confidence limits, which are about 3 times larger than the standard error.

Hydrolysis of $(NH_3)_5CoNHSO_2NH_2^{2+}$. The hydrolysis of the sulfamido complex was found to follow the rate law

$$\frac{-\mathrm{d}\ln[(NH_3)_5CoNHSO_2NH_2]}{\mathrm{d}t} = k_{obsd} = \frac{a[H^+]}{b + [H^+]} \quad (1)$$

The experimental results are listed in Table I, where they are compared to results of a least-squares best fit to eq 1. The product analysis resulted in (95 ± 2)% of the cobalt being recovered from the ion-exchange resin and characterized spectrophotometrically as $(NH_3)_5CoOH_2^{3+}$.

These results are consistent with Co–N bond breaking and with the reaction scheme of eq 2, The rate law for this

$$(NH_3)_5CoNHSO_2R^{2+} + H^+ \underset{K_a}{\rightleftharpoons} (NH_3)_5CoNH_2SO_2R^{3+}$$

$$(NH_3)_5CoNHSO_2R^{2+} \xrightarrow{k_1} (NH_3)_5CoOH_2^{3+} + RSO_2NH^-$$

$$(NH_3)_5CoNH_2SO_2R^{3+} \xrightarrow{k_2} (NH_3)_5CoOH_2^{3+} + RSO_2NH_2 \quad (2)$$

mechanism is shown by eq 3, which is equivalent to eq 1 with

$$\frac{-\mathrm{d}\ln[(NH_3)_5CoNHSO_2R^{2+}]}{\mathrm{d}t} = k_{obsd} = \frac{k_1K_a + k_2[H^+]}{K_a + [H^+]} \quad (3)$$

$a = k_2$ and $b = K_a$ if $k_1K_a \ll k_2[H^+]$. A least-squares fit of the data in Table I to eq 3 indicates that $k_1 << 1 \times 10^{-5}$ s^{-1} at 25 °C and cannot be reliably established. The first step of eq 2 could be due to protonation at the oxygen atom rather than the coordinated nitrogen; however, the precedent of the similar sulfamato complex, which undergoes protonation at the nitrogen atom,[19] makes oxygen protonation seem unlikely. Furthermore, protonation at one of the oxygen atoms would not be expected to have such a large effect on the rate of Co–N bond breaking. For example, $(NH_3)_5CoPO_4H_2^{2+}$ undergoes aquation ($k = 1.57 \times 10^{-5}$ s^{-1} at 60 °C) at a rate just 15 times greater than that of $(NH_3)_5CoPO_4H^+$ ($k = 1.05 \times 10^{-6}$ s^{-1} at 60 °C), suggesting that protonation at a remote oxygen does not significantly affect the rate of aquation.[24] Nitrogen protonation is also consistent with the large increase in K_a of the ligand upon coordination to cobalt(III), an increase similar to that observed for the sulfamato complex.[19] In addition it has been observed that the peak in the visible spectrum of the sulfamido complex shifts from 501 nm in water to 490 nm in 1.00 M $HClO_4$. These observations at 15 °C were made by scanning the 450–550-nm region every 75 s while hydrolysis was occurring. The sulfamido complex is predicted to be about 60% protonated under these conditions, so the protonated form must have an absorption maximum at <490 nm. The shift in wavelength is consistent with protonation at coordinated nitrogen.[19,20]

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Table II. Hydrolysis Kinetic Data for $(NH_3)_5CoNHSO_2C_6H_4CH_3^{2+}$ in 1.00 M $LiClO_4$-$HClO_4$[a]

temp, °C	[H⁺], M	10^3k_{obsd}, s^{-1} obsd[b]	calcd[c]
14.9	0.100	0.696	0.676
14.8	0.200	1.40	1.35
14.8	0.400	2.71	2.70
14.8	0.800	5.08	5.40
25.1	0.104	2.37	2.24
25.1	0.202	4.55	4.35
25.1	0.399	8.67	8.60
25.1	0.794	16.3	17.1
35.0	0.101	6.34	6.32
34.9	0.200	13.0	12.6
34.9	0.302	19.0	19.0
34.8	0.400	24.2	25.1

[a] The cobalt(III) concentration was (2.4–3.2) × 10^{-4} M. [b] Values are the average of at least two runs. [c] Calculated from eq 4 with 10^2c = 0.676 ± 0.024, 2.15 ± 0.07, and 6.28 ± 0.14 M^{-1} s^{-1} at 14.8, 25.1, and 34.9 °C, respectively. Errors are as in Table I.

Table III. Hydrolysis Kinetic Data for $(NH_3)_5CoNHSO_2C_6H_4NO_2^{2+}$ in 1.00 M $LiClO_4$-$HClO_4$[a]

temp, °C	[H⁺], M	10^3k_{obsd}, s^{-1} obsd[b]	calcd[c]
14.9	0.100	0.196	0.192
14.9	0.200	0.392	0.384
14.9	0.400	0.780	0.767
14.9	0.800	1.485	1.53
25.1	0.100	0.594	0.571
25.1	0.200	1.19	1.14
25.0	0.400	2.32	2.28
25.0	0.800	4.40	4.57
25.0	1.00	5.44	5.71
35.1	0.100	1.71	1.59
34.9	0.200	3.26	3.19
35.0	0.400	6.43	6.37
35.0	0.800	12.0	12.7

[a] The cobalt(III) concentration was (3.3–5.7) × 10^{-5} M. [b] Values are the average of at least two runs. [c] Calculated from eq 4 with 10^2c = 0.192 ± 0.007, 0.571 ± 0.017, and 1.59 ± 0.06 M^{-1} s^{-1} at 14.9, 25.0, and 35.0 °C, respectively. Errors are as in Table I.

Hydrolysis of $(NH_3)_5CoNHSO_2C_6H_4X^{2+}$ (X = CH_3, NO_2). Both the *p*-toluenesulfonamido and *p*-nitrobenzenesulfonamido complexes hydrolyze according to the rate law

$$\frac{-\mathrm{d}\ln[(NH_3)_5CoNHSO_2C_6H_4X^{2+}]}{\mathrm{d}t} = k_{obsd} = c[H^+] \quad (4)$$

Typical experimental results are given in Tables II and III, along with least-squares best-fit values. Product analysis studies over a broad range of acid concentrations resulted in (101 ± 4)% ligand being recovered as *p*-toluenesulfonamide or *p*-nitrobenzenesulfonamide. The sulfonamides are easily distinguished from the corresponding sulfonic acids by their electronic spectra in acid and base. In both cases, (96 ± 8)% of the cobalt(III) was recovered as $(NH_3)_5CoOH_2^{3+}$.

Table IV. Summary of Hydrolysis Kinetic Results for $[(NH_3)_5CoNHSO_2\text{-}R]^{2+}$ Complexes in 1.00 M $LiClO_4$-$HClO_4$

ligand	constant[a] (25 °C)	$\Delta H^{\ddagger}$,[b] kcal mol^{-1}	$\Delta S^{\ddagger}$,[b] cal mol^{-1} deg^{-1}
$NHSO_2C_6H_4CH_3^-$	k_2/K_a = 2.16×10^{-2} [c]	19.0 ± 0.5	−2.5 ± 1.5
$NHSO_2C_6H_4NO_2^-$	k_2/K_a = 5.73×10^{-3} [c]	18.0 ± 0.5	−8.4 ± 1.7
$NHSO_2NH_2^-$	$k_2 = 1.32 \times 10^{-2}$ [d] $K_a = 0.55$[e]	21.7 ± 1.1 2.7 ± 1.4[f]	5.5 ± 3.7 7.9 ± 4.7[f]

[a] Values calculated at 25 °C from appropriate ΔH and ΔS values retaining extra figures in the recalculation. [b] Errors are 95% confidence limits and are about 3 times larger than one standard error. [c] Units are M^{-1} s^{-1}. [d] Units are s^{-1}. [e] Units are M. [f] Values are ΔH° and ΔS°.

Therefore, these reactions proceed with Co–N bond breaking.

These results are consistent with the reaction scheme of eq 2, with R = $C_6H_4CH_3$ and $C_6H_4NO_2$, respectively, and the rate law in eq 3, with $c = k_2/K_a$, if $k_1K_a \ll k_2[H^+]$ and $K_a \gg [H^+]$. A least-squares analysis of the data in Tables II and III indicates that at 25 °C $k_1(CH_3)$ and $k_1(NO_2)$ are less than 3×10^{-4} and 6×10^{-5} s^{-1}, respectively, and cannot be reliably established in either case. It may be noted in Tables II and III that there is a tendency for the calculated values to be too small at low $[H^+]$ and too large at high $[H^+]$. The deviations are consistent with K_a values in the range of 5–10 M, but the deviations are too small to permit a realistic estimate of K_a for the coordinated aromatic sulfonamides. If it is assumed that a >15% deviation from eq 4 would be real, then lower limits of 5.3 and 6.6 M can be given to K_a for the *p*-CH_3 and *p*-NO_2 complexes, respectively.

The data for the temperature dependence of the rates for the three complexes have been fitted to the usual transition-state theory and thermodynamic equations. The results are summarized in Table IV.

Kinetic data for the aquation of some pentaammine-cobalt(III) complexes are collected in Table V. Only lower limits can be given for the rate constants for the aromatic sulfonamides because lower limits were established for their K_a values. In any case, it is clear that the sulfamide and sulfonamide complexes have relatively large rate constants for hydrolysis in aqueous acid. In fact, the sulfonamides may hydrolyze about as rapidly as the perchlorato complex. From a practical point of view this means that the sulfamide and sulfonamide complexes must be prepared, recrystallized, and kept in neutral or alkaline solutions where they are stable for hours. But in acidic solution they hydrolyze in minutes or seconds depending on the acidity.

The acid lability of these complexes is consistent with simple ligand basicity arguments based on the behavior of the sulfamato complex. The basicity of the ligand toward cobalt(III) might be expected to parallel the basicity toward the proton as measured by the reaction

$$(NH_3)_5CoNH_2SO_2R \overset{K_a}{\rightleftharpoons} (NH_3)_5CoNHSO_2R + H^+ \quad (5)$$

For the sulfamato complex[19] (R ≡ O^-), $K_a = 2 \times 10^{-6}$ M, while for the sulfamido complex (R ≡ NH_2), $K_a = 0.55$ M. Thus, one might expect the hydrolysis rate constant of the sulfamido complex to be larger than that of the sulfamato complex by $0.55/(2 \times 10^{-6}) \approx 3 \times 10^5$, while at 25 °C the rate constant ratio actually is 5×10^2. Of course this argument is very simplistic, but it indicates that there is no need for any special effect to explain the kinetic lability of the sulfamide and sulfonamide complexes in aqueous acid.

Table V. Kinetic Results for Hydrolysis of $(NH_3)_5CoL$ Complexes in Aqueous Acid

L	k, s^{-1} (25 °C)	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	ref
ClO_4^-	~0.1			*a*
$NH_2SO_2C_6H_4CH_3$	≳0.11			this work
$NH_2SO_2C_6H_4NO_2$	≳0.038			this work
$F_3CSO_3^-$	0.027			*a*
$NH_2SO_2NH_2$	0.013	21.7	5.5	this work
$OP(OCH_3)_3$	2.5×10^{-4}			*b*
$NH_2SO_3^-$	2.6×10^{-5}	24.2	1.4	*c*
NO_3^-	2.0×10^{-5}	24.3	1.9	*d*
$OS(CH_3)_2$	1.8×10^{-5}	24.6	2.3	*e*
SO_4^{2-}	8.9×10^{-7}	22.7	−10	*f*

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The present results have some bearing on the coordination chemistry of sulfonamides and carbonic anhydrase. It is clear that the sulfonamide anion perfers to bond through nitrogen to the metal. Furthermore, the neutral sulfonamides are not strongly bonded by the metal. It would be useful to be able to estimate the pK_a of metal-bound sulfonamides in carbonic anhydrase. This could be done by comparison of the pK_a of the cobalt(III) sulfonamide complexes with those of $(NH_3)_5CoOH_2^{3+}$ (pK_a ~6)[22] and (enzyme) $ZnOH_2$. Unfortunately, the latter value is not available unambiguously. The enzyme has a pK ~7 involved in catalytic activity, but it is not clear if this is for ionization of a histidine or a metal-bound water.[25,26] In any case, the high acidity of $(NH_3)_5CoNH_2SO_2C_6H_4X^{3+}$ is consistent with complete ionization of the enzyme–sulfonamide complex at and above physiological pH values.

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Registry No. $[(NH_3)_5CoNHSO_2NH_2]BrClO_4$, 78891-49-3; $[(NH_3)_5CoNHSO_2C_6H_4CH_3](ClO_4)_2$, 78891-47-1; $[(NH_3)_5CoNHSO_2C_6H_4NO_2](ClO_4)_2$, 78891-45-9; $[(NH_3)_5CoO_3SCF_3)](O_3SCF_3)_2$, 75522-50-8; $[(NH_3)_5CoOH_2](ClO_4)_3$, 13820-81-0.

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