

- (14) All computations were performed using a locally modified version of XRAY 67: J. M. Stewart University of Maryland, crystallographic computer program system.
- (15) $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$, $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.
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Trans Effect in Octahedral Complexes. 3. Comparison of Kinetic and Structural Trans Effects Induced by Coordinated Sulfur in Sulfito- and Sulfinatopentaamminecobalt(III) Complexes^{1,2}

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The synthesis and characterization of arylsulfinatopentaamminecobalt(III) complexes are described. Single-crystal x-ray structure analyses of (*p*-toluenesulfinato-*S*)pentaamminecobalt(III) perchlorate monohydrate and (sulfito-*S*)pentaamminecobalt(III) chloride monohydrate, refined to conventional *R* factors of 0.039 and 0.028, respectively, are reported. Both cobalt(III) centers are ligated by one sulfur and five nitrogen atoms in a configuration that closely approximates octahedral. The salient structural feature of both complexes is that the Co-N bond trans to sulfur is significantly longer than the average of the cis Co-N bonds in the same complex. In the sulfito complex, this sulfur-induced structural trans effect (STE) is 0.089 (3) Å. In [(NH₃)₅CoS(O)₂C₆H₄CH₃]²⁺, the STE is 0.054 (12) Å. Two other sulfinato complexes have STE's of 0.049 (5) and 0.060 (6) Å, yielding 0.054 (6) Å as the best estimate of the sulfinato STE. Thus the sulfito STE is significantly larger than the sulfinato STE, Δ(STE) = 0.035 (7) Å. The rates of ligation of [(NH₃)₅CoSO₃]⁺, [(NH₃)₅CoS(O)₂C₆H₄CH₃]²⁺, and [(NH₃)₅CoS(O)₂C₆H₅]²⁺ by thiocyanate, under identical conditions, as a function of [NH₃], [SCN⁻], and temperature (*p*-toluene complex at 25 °C only) are reported. With NH₃ and SCN⁻ present in pseudo-first-order excess, all reactions are first-order in cobalt complex and the observed first-order rate constant *k*_{obsd} has the form *k*_{obsd} = (*a* + *bc*[SCN⁻]/[NH₃]) / (1 + *c*[SCN⁻]/[NH₃]). This and other evidence are interpreted in terms of a limiting S_N1 mechanism governing labilized ligation at the coordination site trans to sulfur. The salient kinetic features of these reactions are that all complexes exhibit a significant kinetic trans effect (KTE); the KTE exerted by SO₃²⁻ is more than 2 orders of magnitude greater than that exerted by RSO₂⁻, and this difference in KTE's resides in a significantly lower Δ*H*^{*} for the sulfito reaction (the effect of which is partially offset by a less positive Δ*S*^{*}). The lower Δ*H*^{*} for dissociation of the NH₃ trans to SO₃²⁻ is qualitatively correlated with the greater STE exerted by SO₃²⁻. Treatment of this correlation within a simple harmonic oscillator model leads to 3.2 Å as an estimate of the distance to which a cobalt(III)-ligand bond must be stretched in order to achieve a dissociative transition state; this value is in good agreement with an independent estimate obtained from volume of activation measurements. Other interrelations between sulfur-induced KTE's and STE's are discussed.

Introduction

Experiments on a wide variety of complexes have shown that when the S-bonded sulfito ligand (SO₃²⁻) is coordinated to cobalt(III), it exerts a marked kinetic trans effect (KTE); i.e., it labilizes the ligand situated trans to it.¹⁻⁸ Halpern and co-workers^{4,5} first detailed the kinetics of ligand substitution trans to SO₃²⁻ in the [(NH₃)₅CoSO₃]⁺ system, showing that the process occurs via a limiting S_N1 mechanism and that only one ammonia ligand is labilized. In a preliminary communication,⁹ two of us have reported that the trans Co-N bond length in [(NH₃)₅CoSO₃]⁺ is significantly greater than the average of the cis Co-N bond lengths, and thus SO₃²⁻ also induces a significant ground-state structural trans effect (STE) in this system. This observation argues strongly for the hypothesis that the KTE documented by Halpern⁴ results at least partially from a ground-state weakening of the trans cobalt-ligand bond. Two recent observations have indicated

that in cobalt(III) complexes the extent of the sulfur-induced KTE may be qualitatively correlated with the extent of the concomitant STE: (1) S-bonded sulfinic acids (RSO₂⁻) exert a KTE in bis(dimethylglyoximate)cobalt(III) complexes which is smaller than that exerted by SO₃²⁻ in the same complexes;^{1,2} (2) the S-bonded sulfinic acid in [(en)₂Co(S(O)₂CH₂CH₂NH₂)]²⁺ exerts an STE which is smaller than that exerted by SO₃²⁻ in [(NH₃)₅CoSO₃]⁺.¹⁰ In order to quantitatively correlate the STE and KTE exerted by RSO₂⁻ and SO₃²⁻ we have undertaken an evaluation of these effects within analogous complexes and for a variety of reasons have chosen the pentaamminecobalt(III) system for study. In this paper we report the synthesis of arylsulfinatopentaamminecobalt(III) complexes, the detailed x-ray characterization of one of these sulfinato complexes as well as of the sulfito complex which hitherto has only been briefly described,⁹ a detailed comparison (including temperature dependencies) of the rates of ligation

of sulfinato- and sulfitopentaamminecobalt(III) complexes, and the resulting quantitative evaluation of the extent to which the STE is manifested in the activation parameters governing the KTE.

Experimental Section

Reagents and Analyses. All common laboratory chemicals were of reagent grade unless otherwise noted. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Water was triply distilled in an all-glass system and solutions for kinetic studies were prepared from this water. Perchloric acid solutions were prepared from G. F. Smith doubly distilled 70–72% HClO₄. Lithium perchlorate solutions were prepared by exact neutralization of Baker Ultrex grade Li₂CO₃.¹¹ Solutions of ammonia were standardized by addition of excess boric acid and titration with standardized HCl using bromocresol green indicator. Solutions of lithium thiocyanate were standardized by Volhard titration.

(Sulfito-S)pentaamminecobalt(III) Salts, [(NH₃)₅CoSO₃]X, X⁻ = Cl⁻, ClO₄⁻. These complexes were prepared as previously described.^{9,12} Crystals of the chloride salt suitable for x-ray structural analysis were grown from an ethanol–water solution containing 2 M NH₃ and 1 M NH₄Cl. This material is shown to be the monohydrate by x-ray analysis (vide infra) and TGA: calculated weight loss for H₂O 6.5%; observed loss 6.9 ± 0.2% at 92 °C. Elemental analysis indicated the correct atom ratios, but approximately 5% inert material and/or moisture in the sample submitted for analysis. Anal. Calcd for [(NH₃)₅CoSO₃]Cl·H₂O: S/Cl/N/H/Co = 1/1/5/17/1. Found: S/Cl/N/H/Co = 1.00/1.00/4.95/17.7/1. The perchlorate salt was purified for use in kinetic studies by three crystallizations from warm 3 M NH₃ containing an appropriate amount of NaClO₄. Visible–UV spectral parameters for the perchlorate salt (see Table I) are in good agreement with those reported by Siebert and Wittke.¹²

(*p*-Toluenesulfinato-S)pentaamminecobalt(III) Perchlorate Monohydrate, [(NH₃)₅CoS(O)₂C₆H₄CH₃](ClO₄)₂·H₂O. In a typical preparation 14.83 g (32 mmol) of aquopentaamminecobalt(III) perchlorate¹³ and 5.73 g (32 mmol) of sodium *p*-toluenesulfinate (Aldrich) were dissolved in 100 mL of dimethyl sulfoxide and the solution was heated with stirring at 60 °C for 1 h during which time the solution changed color from red to dark brown. Dilution of the reaction mixture to 1 L with 2-propanol led to a dark brown oil which, after cooling, could easily be separated from the supernatant and dissolved in 80 mL of 6 M NH₃. The resulting solution was filtered and warmed to ca. 40 °C, and then saturated aqueous NaClO₄ solution was added till incipient precipitation; slow cooling of this solution yielded a crude crystalline product. This crude product was purified by dissolution in acetone, separation from acetone-insoluble impurities, and then precipitation by addition of diethyl ether. This purified product was then dissolved in a minimum amount of warm 6 M NH₃, the solution filtered, and an equal volume of saturated aqueous NaClO₄ solution added. This procedure yielded a solid mass of fibrous, yellow-brown crystals suspended in the crystallizing medium; on standing, these crystals slowly (3 days to 1 week) transmuted into well-formed, deep brown crystals suitable for single-crystal x-ray analysis (yield 3.4 g, 21%). Anal. Calcd for [(NH₃)₅CoS(O)₂C₆H₄CH₃](ClO₄)₂·H₂O: Co, 11.42; S, 6.21; N, 13.57; C, 16.29; H, 4.67. Found (crystalline material): Co, 11.74; S, 6.22; N, 14.09; C, 16.72; H, 4.88.

(Benzenesulfinato-S)pentaamminecobalt(III) Perchlorate, [(NH₃)₅CoS(O)₂C₆H₅](ClO₄)₂. This material was prepared analogously to the toluene complex above, except that sodium benzenesulfinate (Aldrich) was used as starting material. This complex is not soluble in acetone and was therefore purified by three crystallizations from a 1:1 6 M NH₃-saturated aqueous NaClO₄ solution. Anal. Calcd for [(NH₃)₅CoS(O)₂C₆H₅](ClO₄)₂·2H₂O: Co, 11.33; S, 6.16; N, 13.46; C, 13.85; H, 4.65. Found: Co, 11.85; S, 5.98; N, 13.73; C, 13.39; H, 4.17.

Equipment. Visible–UV and infrared spectra were recorded respectively on Cary 14 and Beckman IR-18A spectrophotometers at ambient temperature. Kinetic data were obtained on a Cary 118B spectrophotometer equipped with a thermostated sample compartment that maintained temperatures to ±0.1 °C, the temperature being known with an accuracy of ±0.2 °C. ¹H NMR spectra were obtained on Varian T-60 and A-60 instruments. X-ray data were collected with a Syntex P1 diffractometer, equipped with a graphite monochromator and molybdenum target tube (Mo Kα, λ 0.71069 Å), at ambient temperature. Computer calculations were performed on an

IBM 370/168, or AMDAHL 470/V6, located at the University of Cincinnati.

Kinetic Procedures and Data Analysis. Blank experiments showed that the sulfinato complexes decompose with a half-life of ca. 40 h in 1.0 M NH₃ (25 °C, no SCN⁻ present). This slow decomposition does not interfere directly with the ligation reaction of interest (vide infra), but it does require that stock solutions of the sulfinato complexes be prepared immediately prior to use. Similarly, Palmer¹⁴ reported that slow decomposition of the sulfito complex does not interfere with its ligation reactions. All kinetic experiments were conducted in aqueous solutions with ionic strength maintained at 1.00 ± 0.01 M with LiClO₄ and [NH₄⁺] maintained equal to [NH₃] to yield a constant [OH⁻] of about 2 × 10⁻⁵ M; the concentration of cobalt complex was ca. 3 × 10⁻³ M. Immediately prior to an experiment, a weighed sample of pentaammine complex was dissolved in buffered 0.030 M NH₃. An aliquot of this solution plus appropriate volumes of stock NH₃, HClO₄, and LiClO₄ solutions and water was then pipetted into a 1-cm spectrophotometric cell and the resulting solution allowed to reach temperature equilibrium. The kinetic experiment was initiated by rapid injection of an aliquot of LiSCN stock solution. Reactions were monitored for at least 3 half-lives at the absorption maximum (visible region) for the starting complex (see Table I). In some experiments an infinite-time measurement (OD_∞) could be determined directly and in these cases plots of log (OD_∞ - OD_{*t*}) vs. time were linear for at least 95% of the reaction indicating that the system follows first-order kinetics. However, in most experiments OD_∞ could not be obtained due to slow decomposition of the initial and product complexes. Therefore the previously described¹⁵ LASL nonlinear least-squares program was employed to determine the values of *k*_{obsd}, OD₀, and OD_∞ which best fit the OD_{*t*}, *t* data within the first-order rate expression

$$OD_t = OD_\infty - (OD_\infty - OD_0)e^{-k_{\text{obsd}}t} \quad (1)$$

where the subscripts on OD indicate the time of the optical density reading and *k*_{obsd} is the observed first-order rate parameter. To maintain internal consistency, all kinetic data were treated by this nonlinear technique; in all subsequent calculations values of *k*_{obsd} were weighted by 1/σ_{*k*}² where σ_{*k*} is the standard deviation of *k*_{obsd} resulting from the least-squares treatment. For each kinetic experiment, σ_{OD} was calculated based on the discrepancies between observed values of OD_{*t*} and those calculated from eq 1 using optimized values of OD₀, OD_∞, and *k*_{obsd}. The maximum value of σ_{OD} was 0.0029 optical density unit; the average was 0.0014 optical density unit (total OD change was ca. 0.16 unit). Unless otherwise noted, all uncertainties reported in this work are standard deviations.

X-Ray Characterization of [(NH₃)₅CoS(O)₂C₆H₄CH₃](ClO₄)₂·H₂O. A dark brown tablet of approximate dimensions 0.37 × 0.22 × 0.42 mm was mounted on the diffractometer and our usual procedures¹⁶ were followed to check the crystal quality (three axial-rotation photographs and mosaic-scan measurements), determine unit cell constants (15 reflections), and measure intensities. The crystal is of the monoclinic class with *a* = 14.837 (6) Å, *b* = 6.910 (9) Å, *c* = 19.576 (9) Å and β = 101.44 (6)°. With *Z* = 4, *d*_{calcd} = 1.74, and *d*_{measd} = 1.73 (3) g cm⁻³. Inspection of the intensity data set (vide infra) revealed the systematic absences *h* = odd for *h*0*l* and *k* = odd for 0*k*0; this suggests the space group¹⁷ P2₁/a (nonstandard setting of P2₁/c, No. 14). The rate for the θ/2θ scan varied between 1.0 and 6.0°/min depending on the intensity of the reflection being measured. The scan ranged from 1.2° in 2θ below the calculated Kα₁ peak position to 1.3° above that calculated for Kα₂. Four standard reflections were monitored to check crystal stability and to account for long-term drift; the drift correction varied from 1.017 to 0.979 and was random in behavior. Absorption corrections (linear absorption coefficient μ = 13.7 cm⁻¹) were applied¹⁸ with transmission coefficients ranging from 0.68 to 0.78. A series of Ψ scans was conducted for each of the standard reflections to ensure the validity of the calculated corrections. Within the sphere 2θ < 46°, 3463 reflections were measured in the forms *hkl* and *hk̄l*; from these, 2590 unique reflections were obtained by averaging.¹⁹ Of these, 2384 had *I* > 2σ(*I*), where *p*, the ignorance factor used to calculate¹⁶ σ(*I*), was set equal to 0.04.

X-Ray Characterization of [(NH₃)₅CoSO₃]Cl·H₂O. A dark brown crystal of approximate dimensions 0.08 × 0.12 × 0.12 mm was generally characterized as above, with the following differences in procedure and data. Preliminary precision photographs on a larger crystal exhibited systematic absences *l* = odd for *h*0*l* and *k* = odd

for $0k0$, indicating the space group¹⁷ $P2_1/c$, No. 14. Cell constants (13 reflections) are $a = 12.127$ (5) Å, $b = 6.651$ (2) Å, $c = 12.296$ (4) Å, and $\beta = 95.75$ (2)°. With $Z = 4$, $d_{\text{calcd}} = 1.87$, and $d_{\text{measd}} = 1.87$ (2) g cm⁻³. The $\theta/2\theta$ scan rate varied between 1.0 and 24.0°/min, and the scan ranged from 1.0° in 2θ below the calculated $K\alpha_1$ peak position to 1.0° above that calculated for $K\alpha_2$. The drift correction varied from 1.019 to 0.985 and was random in behavior. Absorption corrections were not applied since $\mu = 22.68$ cm⁻¹ and the maximum relative error in the measured intensities was estimated to be less than 4%. Within the sphere $2\theta < 56^\circ$, 2441 reflections were measured in the forms hkl and $\bar{h}k\bar{l}$; from these, 2355 were obtained by averaging.¹⁹ Of these, 1977 had $I > 2\sigma(I)$ with p set equal to 0.02.

Structure Solution and Refinement of [(NH₃)₅CoS(O)₂C₆H₄CH₃](ClO₄)₂·H₂O. This structure was solved using normal Patterson techniques and refinement proceeded without difficulty. The hydrogen atoms of the benzene ring were located at their calculated positions; the hydrogen atoms of the ammonia ligands and the methyl group were placed at tetrahedral positions²⁰ such that they gave the closest possible agreement with the peak positions found from a difference map ($C-H = 0.97$ Å; $N-H = 0.87$ Å). All hydrogen atoms were assigned isotropic temperature parameters²¹ of $B = 4.0$ Å². In the final cycles of least-squares refinement, 245 parameters were varied including the overall scale factor, positional parameters, and anisotropic thermal parameters for all nonhydrogen atoms but excluding hydrogen atom positional and thermal parameters. Convergence was achieved with $R_1 = 0.039$ and $R_2 = 0.041$.²² In the last cycle of refinement the maximum shift per error was 0.026 and the average shift per error was 0.005. A final difference map showed the largest peak to be less than 0.06 times the height of a carbon atom. The final error of an observation of unit weight was 1.49. Neutral atom scattering curves as given by Cromer²³ were used for Co, S, Cl, O, N, and C; those of Stewart²⁴ were used for H. Anomalous dispersion corrections²⁵ were made for Co, S, and Cl. The values of $|F_o|$ and F_c are listed in Table A.²⁶

Structure Solution and Refinement of [(NH₃)₅CoSO₃](Cl·H₂O). Solution and refinement of this structure were as above, with the following differences in procedures and data. In the final cycles of least-squares refinement 160 parameters were varied including the overall scale factor, positional parameters for all atoms, and anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atom isotropic thermal parameters²¹ were held fixed at $B = 4.0$ Å². Refinement converged with $R_1 = 0.028$ and $R_2 = 0.032$.²² In the final cycle of refinement the maximum shift per error was 0.13 and the average shift per error was 0.03. A final difference map was featureless; the largest two peaks (ca. 0.04 times the height of a nitrogen atom) were within 1.0 Å of the cobalt atom. The final error of an observation of unit weight was 1.22. The values of $|F_o|$ and F_c are listed in Table B.²⁶

Results

Characterization of Sulfinatopentaamminecobalt(III) Complexes. In addition to the x-ray structure analysis described below, the new sulfinato complexes prepared in this study are characterized by (1) elemental analysis of isolated salts which give empirical compositions in agreement with those predicted (see Experimental Section), (2) cation-exchange elution characteristics which are consistent with the assigned formal charge, and (3) the spectral parameters listed in Table I. In this latter category, the ¹H NMR spectra contain peaks which confirm the presence of the organic moieties, and the visible-UV spectra exhibit d-d bands characteristic of cobalt(III) complexes as well as intense ligand-to-metal charge transfer (LTMCT) bands which characteristically arise from coordination of sulfur to a potentially oxidizing center.²⁷

Crystal Structures. In this section most of the x-ray data are presented in pairs of analogous tables and figures, the first member of each pair containing data for [(NH₃)₅CoS(O)₂C₆H₄CH₃](ClO₄)₂·H₂O and the second member containing data for [(NH₃)₅CoSO₃](Cl·H₂O). Final fractional atomic positional parameters, and their estimated standard deviations, for nonhydrogen atoms are given in Tables II and III. The corresponding anisotropic thermal parameters may be found in Tables C²⁶ and D,²⁶ the root-mean-square displacements

Table I. Spectral Parameters for Sulfito- and Sulfinatocobalt(III) Complexes

| A. Visible-UV ^a | | | | |
|--|---|----------------------------|----------------------------|-----|
| Complex ^b | Medium | λ_{max} (e) | λ_{max} (e) | Ref |
| (NH ₃) ₅ CoSO ₃ ⁺ | 3 M NH ₃ | 456 (150) | 278 (18 900) | c |
| (NH ₃) ₅ CoSO ₃ ⁺ | 1 M NH ₃ | 457 (148) | 279 (17 800) | 12 |
| (NH ₃) ₅ CoS(O) ₂ C ₆ H ₅ ²⁺ | 3 M NH ₃ | 465 (204) | 303 (13 400) | c |
| (NH ₃) ₅ CoS(O) ₂ C ₆ H ₄ CH ₃ ²⁺ | 3 M NH ₃ | 463 (221) | 303 (13 500) | c |
| (en) ₂ Co(S(O) ₂ CH ₂ -CH ₂ NH ₂) ₂ ²⁺ | 0.1 M HClO ₄ | 432 (220) | 288 (14 200) | 10 |
| B. ¹ H NMR ^d | | | | |
| Complex ^b | τ (shape, integration, assignment) | | | |
| (NH ₃) ₅ CoS(O) ₂ C ₆ H ₅ ²⁺ | 2.23-2.42 (m, 5 H, C ₆ H ₅) 6.28 (br, \approx 1 H, trans NH ₃) 7.17 (br, 12 H, cis NH ₃) | | | |
| (NH ₃) ₅ CoS(O) ₂ C ₆ H ₄ CH ₃ ²⁺ | 2.22-2.67 (m, 4 H, C ₆ H ₄) 6.28 (br, \approx 2 H, trans NH ₃) \approx 6.6 (br, \approx 1 H, trans NH ₃) 7.17 (br, 12 H, cis NH ₃) 7.57 (s, 3 H, CH ₃) | | | |
| C. IR ^e | | | | |
| Complex ^f | ν , intensity, shape | | | |
| (NH ₃) ₅ CoSO ₃ ⁺ | 3320-3020, ^g 1623 m, b, 1302 s, 1105 vs, 994 s, 982 s, 852 m, 808 m, 745 w, 724 w, 640 sh, 631 vs, 525 m, 478 w, 440 w, 406 w | | | |
| (NH ₃) ₅ CoS(O) ₂ C ₆ H ₅ ²⁺ | 3330-3030, ^g 1600 m, b, 1460 s, 1440 s, 1375 s, 1365 sh, 1345 sh, 1335 m, 1315 vs, 1185 s, 1090 s, 1070 m, 1045 s, 1040 sh, 1020 w, 840 b, 750 m, 720 w, 700 s, 692 s | | | |
| (NH ₃) ₅ CoS(O) ₂ C ₆ H ₄ CH ₃ ²⁺ | 3340-3020, ^g 1585 m, b, 1450 s, b, 1380 s, 1325 m, b, 1175 s, 1170 s, 1115 s, 1080 s, 1035 s, 1010 s, 845 sh, 820 m, 975 w, 740 sh, 725 w, 710 w, 640 s | | | |

^a λ in nm, ϵ in M⁻¹ cm⁻¹. ^b As perchlorate salts. ^c This work. ^d In Me₂SO-d₆ with Me₄Si as internal reference; τ values in ppm; s = singlet, m = multiplet, br = broad. ^e In Nujol mulls; ν values in cm⁻¹; v = very, s = strong, m = medium, w = weak, b = broad, sh = shoulder. ^f Sulfito complex as chloride salt; sulfinato complexes as iodide salts. ^g Very broad band in this range.

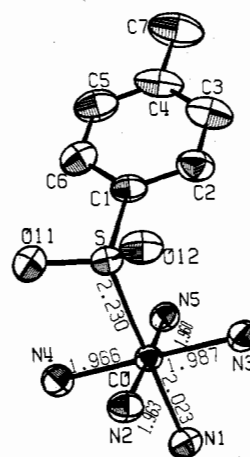


Figure 1. Perspective view of [(NH₃)₅CoS(O)₂C₆H₄CH₃]²⁺. The ellipsoids represent 50% probability, hydrogen atoms have been omitted for clarity, and selected bond lengths are given in Å.

calculated therefrom are collected in Tables IV and V, and the associated ellipsoids for the complex cations are shown in

Table II. Fractional Atomic Positional Parameters^{a,b} for $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

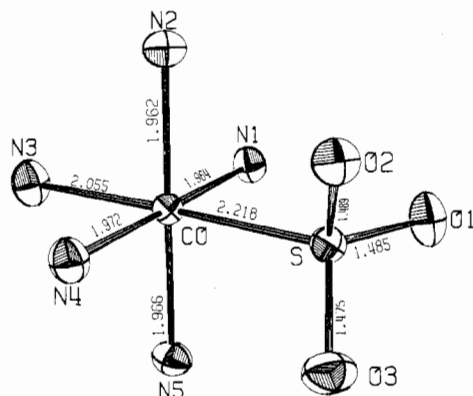
| Atom | x | y | z |
|--------------------|-------------|-------------|-------------|
| Co | 0.37615 (2) | 0.53966 (8) | 0.31056 (3) |
| S | 0.29616 (5) | 0.7976 (2) | 0.26457 (6) |
| N(1) | 0.4522 (2) | 0.3138 (6) | 0.3556 (2) |
| N(2) | 0.3959 (2) | 0.6786 (6) | 0.3997 (2) |
| N(3) | 0.4893 (2) | 0.6585 (6) | 0.2892 (2) |
| N(4) | 0.2647 (2) | 0.4250 (2) | 0.3338 (2) |
| N(5) | 0.3516 (2) | 0.3918 (5) | 0.2233 (2) |
| O(11) ^c | 0.2067 (2) | 0.7995 (5) | 0.2861 (2) |
| O(12) | 0.3525 (2) | 0.9715 (5) | 0.2845 (2) |
| C(1) | 0.2720 (2) | 0.7957 (6) | 0.1716 (3) |
| C(2) | 0.3426 (2) | 0.8279 (8) | 0.1358 (3) |
| C(3) | 0.3233 (3) | 0.8276 (9) | 0.0635 (3) |
| C(4) | 0.2331 (3) | 0.8009 (8) | 0.0264 (3) |
| C(5) | 0.1648 (3) | 0.7684 (9) | 0.0635 (3) |
| C(6) | 0.1827 (2) | 0.7631 (7) | 0.1359 (3) |
| C(7) | 0.2149 (4) | 0.8077 (11) | -0.0517 (4) |
| Cl(8) | 0.36350 (5) | 0.1621 (2) | 0.51994 (6) |
| O(81) ^c | 0.2743 (2) | 0.1860 (8) | 0.5326 (3) |
| O(82) | 0.3584 (3) | 0.0631 (8) | 0.4566 (3) |
| O(83) | 0.4060 (2) | 0.3478 (6) | 0.5127 (2) |
| O(84) | 0.4178 (3) | 0.0683 (9) | 0.5764 (3) |
| Cl(9) | 0.56457 (6) | 0.2179 (2) | 0.17396 (7) |
| O(91) ^c | 0.6614 (2) | 0.2323 (7) | 0.1910 (2) |
| O(92) | 0.5247 (2) | 0.4094 (6) | 0.1679 (2) |
| O(93) | 0.5307 (3) | 0.1139 (8) | 0.2264 (3) |
| O(94) | 0.5367 (3) | 0.1168 (9) | 0.1106 (3) |
| O(1) | 0.1528 (2) | 0.0843 (6) | 0.3714 (2) |

^a The estimated errors in the last digit are given in parentheses. This form is used throughout. ^b The numbering scheme of the cation is shown in Figure 1. ^c O(1*n*) bound to S; O(8*n*) bound to Cl(8); O(9*n*) bound to Cl(9). O(1) is the oxygen atom of the water molecule.

Table III. Fractional Atomic Positional Parameters^a for $[(\text{NH}_3)_5\text{CoSO}_3]\text{Cl} \cdot \text{H}_2\text{O}$

| Atom | x | y | z |
|------|-------------|--------------|-------------|
| Co | 0.29582 (2) | 1.04210 (4) | 0.11957 (2) |
| Cl | 0.06467 (5) | 0.67174 (10) | 0.33797 (5) |
| S | 0.38609 (4) | 0.75430 (8) | 0.11024 (4) |
| O(1) | 0.5066 (1) | 0.7928 (2) | 0.1114 (2) |
| O(2) | 0.3660 (1) | 0.6304 (2) | 0.2069 (1) |
| O(3) | 0.3430 (2) | 0.6483 (2) | 0.0097 (1) |
| O(4) | 0.0997 (2) | 1.1341 (4) | 0.3854 (2) |
| N(1) | 0.4322 (2) | 1.2024 (3) | 0.1281 (2) |
| N(2) | 0.3102 (2) | 1.0219 (3) | 0.2792 (2) |
| N(3) | 0.2061 (2) | 1.3025 (3) | 0.1261 (2) |
| N(4) | 0.1582 (2) | 0.8834 (3) | 0.1117 (2) |
| N(5) | 0.2825 (2) | 1.0598 (3) | -0.0406 (2) |

^a The numbering scheme for the cation is shown in Figure 2. O(4) is the oxygen atom of the water molecule.

**Figure 2.** Perspective view of $[(\text{NH}_3)_5\text{CoSO}_3]^+$. Specifications as given in Figure 1.

Figures 1 and 2. Bond lengths and angles not involving hydrogen atoms are presented in Tables VI and VII and Tables

Table IV. Rms Displacements (Å) for $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

| Atom | Min | Mean | Max |
|-------|-------|-------|-------|
| Co | 0.147 | 0.164 | 0.167 |
| S | 0.165 | 0.172 | 0.189 |
| N(1) | 0.18 | 0.20 | 0.21 |
| N(2) | 0.16 | 0.19 | 0.21 |
| N(3) | 0.18 | 0.19 | 0.21 |
| N(4) | 0.18 | 0.19 | 0.21 |
| N(5) | 0.17 | 0.18 | 0.19 |
| O(11) | 0.19 | 0.22 | 0.24 |
| O(12) | 0.17 | 0.19 | 0.25 |
| C(1) | 0.15 | 0.18 | 0.22 |
| C(2) | 0.18 | 0.21 | 0.24 |
| C(3) | 0.19 | 0.22 | 0.30 |
| C(4) | 0.17 | 0.19 | 0.31 |
| C(5) | 0.18 | 0.22 | 0.29 |
| C(6) | 0.19 | 0.21 | 0.24 |
| C(7) | 0.20 | 0.24 | 0.37 |
| Cl(8) | 0.185 | 0.199 | 0.225 |
| O(81) | 0.24 | 0.32 | 0.34 |
| O(82) | 0.25 | 0.31 | 0.37 |
| O(83) | 0.23 | 0.25 | 0.29 |
| O(84) | 0.26 | 0.31 | 0.41 |
| Cl(9) | 0.181 | 0.226 | 0.256 |
| O(91) | 0.17 | 0.32 | 0.33 |
| O(92) | 0.23 | 0.26 | 0.30 |
| O(93) | 0.29 | 0.30 | 0.34 |
| O(94) | 0.25 | 0.31 | 0.39 |

Table V. Rms Displacements (Å) for $[(\text{NH}_3)_5\text{CoSO}_3]\text{Cl} \cdot \text{H}_2\text{O}$

| Atom | Min | Mean | Max |
|------|-------|-------|-------|
| Co | 0.114 | 0.120 | 0.129 |
| Cl | 0.164 | 0.188 | 0.219 |
| S | 0.119 | 0.132 | 0.143 |
| O(1) | 0.136 | 0.157 | 0.210 |
| O(2) | 0.125 | 0.163 | 0.178 |
| O(3) | 0.143 | 0.168 | 0.222 |
| O(4) | 0.186 | 0.229 | 0.235 |
| N(1) | 0.129 | 0.136 | 0.160 |
| N(2) | 0.134 | 0.158 | 0.164 |
| N(3) | 0.134 | 0.159 | 0.196 |
| N(4) | 0.140 | 0.151 | 0.168 |
| N(5) | 0.132 | 0.155 | 0.166 |

Table VI. Bond Lengths (Å) for $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

| Cation | | | |
|-------------|-----------|-------------|-----------|
| Co-S | 2.230 (2) | S-C(1) | 1.783 (5) |
| Co-N(5) | 1.960 (4) | C(1)-C(2) | 1.387 (6) |
| Co-N(4) | 1.966 (3) | C(1)-C(6) | 1.388 (5) |
| Co-N(3) | 1.986 (3) | C(2)-C(3) | 1.389 (8) |
| Co-N(2) | 1.963 (4) | C(3)-C(4) | 1.403 (7) |
| Co-N(1) | 2.023 (4) | C(4)-C(5) | 1.377 (8) |
| S-O(11) | 1.469 (3) | C(4)-C(7) | 1.501 (9) |
| S-O(12) | 1.472 (3) | C(5)-C(6) | 1.390 (8) |
| Anions | | | |
| Cl(8)-O(81) | 1.403 (4) | Cl(9)-O(91) | 1.413 (3) |
| Cl(8)-O(82) | 1.404 (6) | Cl(9)-O(92) | 1.445 (4) |
| Cl(8)-O(83) | 1.449 (5) | Cl(9)-O(93) | 1.424 (6) |
| Cl(8)-O(84) | 1.393 (6) | Cl(9)-O(94) | 1.411 (6) |

Table VII. Bond Lengths (Å) for $[(\text{NH}_3)_5\text{CoSO}_3]\text{Cl} \cdot \text{H}_2\text{O}$

| | | | |
|---------|-----------|--------|-----------|
| Co-N(1) | 1.964 (2) | Co-S | 2.218 (1) |
| Co-N(2) | 1.962 (2) | S-O(1) | 1.485 (2) |
| Co-N(4) | 1.972 (2) | S-O(2) | 1.489 (2) |
| Co-N(5) | 1.966 (2) | S-O(3) | 1.475 (2) |
| Co-N(3) | 2.055 (2) | | |

VIII and IX, respectively. Tables E²⁶ and F²⁶ contain hydrogen atom positional parameters, Tables X and XI detail possible hydrogen bonds, and Table G²⁶ lists bond lengths and bond angles resulting from refinement of the hydrogen atom positional parameters in the sulfite structure.

Table VIII. Bond Angles (deg) for $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

| Metal Coordination Angles | | | |
|---------------------------|-----------|-------------------|-----------|
| S-Co-N(1) | 177.3 (4) | N(1)-Co-N(5) | 88.3 (2) |
| S-Co-N(2) | 86.7 (1) | N(2)-Co-N(3) | 90.0 (1) |
| S-Co-N(3) | 89.4 (1) | N(2)-Co-N(4) | 88.6 (1) |
| S-Co-N(4) | 90.6 (1) | N(2)-Co-N(5) | 176.9 (3) |
| S-Co-N(5) | 94.2 (1) | N(3)-Co-N(4) | 178.6 (2) |
| N(1)-Co-N(2) | 90.9 (2) | N(3)-Co-N(5) | 92.9 (1) |
| N(1)-Co-N(3) | 89.4 (1) | N(4)-Co-N(5) | 88.5 (1) |
| N(1)-Co-N(4) | 90.6 (1) | | |
| Ligand Angles | | | |
| Co-S-C(1) | 112.9 (1) | C(2)-C(1)-S | 119.7 (3) |
| Co-S-O(11) | 109.2 (1) | C(6)-C(1)-S | 119.5 (4) |
| Co-S-O(12) | 108.5 (1) | C(1)-C(2)-C(3) | 119.4 (4) |
| O(11)-S-C(1) | 106.5 (2) | C(2)-C(3)-C(4) | 120.7 (5) |
| O(12)-S-C(1) | 105.4 (2) | C(3)-C(4)-C(5) | 118.4 (5) |
| O(11)-S-O(12) | 114.5 (2) | C(4)-C(5)-C(6) | 122.0 (4) |
| C(7)-C(4)-C(5) | 122.7 (5) | C(5)-C(6)-C(1) | 118.7 (4) |
| C(7)-C(4)-C(3) | 118.9 (5) | C(6)-C(1)-C(2) | 120.8 (5) |
| Perchlorate Angles | | | |
| O(81)-Cl(8)-O(82) | 109.1 (3) | O(91)-Cl(9)-O(92) | 109.6 (2) |
| O(81)-Cl(8)-O(83) | 110.9 (3) | O(91)-Cl(9)-O(93) | 110.6 (3) |
| O(81)-Cl(8)-O(84) | 109.3 (3) | O(91)-Cl(9)-O(94) | 110.4 (3) |
| O(82)-Cl(8)-O(83) | 107.1 (3) | O(92)-Cl(9)-O(93) | 108.9 (3) |
| O(82)-Cl(8)-O(84) | 113.4 (3) | O(92)-Cl(9)-O(94) | 109.8 (3) |
| O(83)-Cl(8)-O(84) | 107.1 (3) | O(93)-Cl(9)-O(94) | 107.5 (3) |

Table IX. Bond Angles (deg) for $[(\text{NH}_3)_5\text{CoSO}_3]\text{Cl} \cdot \text{H}_2\text{O}$

| | | | |
|--------------|-----------|-------------|-----------|
| N(1)-Co-N(2) | 89.7 (1) | S-Co-N(1) | 93.1 (1) |
| N(1)-Co-N(3) | 89.2 (1) | S-Co-N(2) | 89.9 (1) |
| N(1)-Co-N(4) | 179.4 (3) | S-Co-N(3) | 177.6 (3) |
| N(1)-Co-N(5) | 90.3 (1) | S-Co-N(4) | 87.4 (1) |
| N(2)-Co-N(3) | 90.8 (1) | S-Co-N(5) | 89.5 (1) |
| N(2)-Co-N(4) | 90.1 (1) | Co-S-O(1) | 110.0 (1) |
| N(2)-Co-N(5) | 179.4 (5) | Co-S-O(2) | 108.5 (1) |
| N(3)-Co-N(4) | 90.3 (1) | Co-S-O(3) | 108.9 (1) |
| N(3)-Co-N(5) | 89.9 (1) | O(1)-S-O(2) | 109.2 (1) |
| N(4)-Co-N(5) | 90.0 (1) | O(1)-S-O(3) | 110.9 (1) |
| | | O(2)-S-O(3) | 109.5 (1) |

Table X. Possible Hydrogen Bonds for $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

| Atoms X-H...Y | H...Y, A | X...Y, ^b A | X-H...Y, ^a deg |
|---------------------------------|-------------|--------------------------|------------------------------|
| N(1), H(13), O(93) | 2.45 | 3.30 | 163 |
| N(1), H(11), O(82) | 2.40 | 3.15 | 146 |
| N(2), H(23), O(81) ^c | 2.25 | 3.07 | 162 |
| N(3), H(32), O(1) ^d | 2.38 | 3.12 | 143 |
| N(3), H(31), O(92) | 2.20 | 3.06 | 169 |
| N(5), H(51), O(91) ^d | 2.15 | 2.89 | 145 |
| N(5), H(52), O(92) | 2.25 | 2.98 | 140 |
| N(5), H(53), O(62) ^e | 2.35 | 3.14 | 152 |

^a X-H...Y > 140°. ^b X...Y < 3.3 Å. ^c Transformed to 1/2 - x, -1/2 + y, 1 - z. ^d 1/2 + x, 1/2 - y, z. ^e x, 1 + y, z.

Both crystal structures involve discrete cationic complexes, anions, and water molecules. The cobalt(III) centers are six-coordinate (five ammonia ligands and the sulfur atom of the sulfito or sulfinate ligand) in a configuration that closely approximates octahedral. The major distortion from octahedral geometry results from steric crowding between an ammonia molecule and one of the groups bonded to sulfur; in $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ the tolyl ring interacts with N(5) causing the sulfur atom to bend away from N(5) and toward N(2) (N-Co-S angles of 94.2 (1) and 86.7 (1)°, respectively); in $[(\text{NH}_3)_5\text{CoSO}_3]^+$ O(1) interacts with N(1) causing the sulfur atom to bend away from N(1) and toward N(4) (N-Co-S angles of 93.1 (1) and 87.4 (1)°, respectively). A structural trans effect (STE) is clearly evident in both complexes. In $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ the average of the four cis Co-N bond lengths is 1.969 (12) Å, the trans Co-N bond length is 2.023 (4) Å, and the resulting STE is

Table XI. Possible Hydrogen Bonds for $[(\text{NH}_3)_5\text{CoSO}_3]\text{Cl} \cdot \text{H}_2\text{O}$

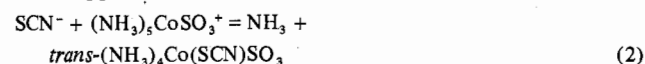
| Atoms X-H...Y | X-H, A | H...Y, A | X...Y, ^a A | X-H...Y, ^b deg |
|--------------------------------|-----------|-------------|--------------------------|------------------------------|
| N(1), H(1), O(1) ^c | 0.95 | 2.20 | 3.12 | 162 |
| N(1), H(2), O(2) ^d | 0.93 | 2.18 | 3.06 | 157 |
| N(2), H(5), O(4) | 0.89 | 2.21 | 3.08 | 167 |
| N(2), H(6), O(1) ^d | 0.73 | 2.36 | 3.07 | 163 |
| N(3), H(7), O(2) ^e | 0.90 | 2.17 | 3.03 | 159 |
| N(3), H(8), O(4) ^f | 0.90 | 2.31 | 3.14 | 153 |
| N(5), H(13), O(4) ^f | 0.87 | 2.23 | 3.08 | 169 |
| N(5), H(14), O(1) ^c | 0.94 | 2.01 | 2.95 | 173 |
| O(4), H(17), Cl | 0.91 | 2.26 | 3.16 | 166 |

^a X...Y < 3.3 Å. ^b Angle at hydrogen atom > 140°. ^c Atom transformed by 1 - x, 2 - y, -z. ^d 1 - x, 1/2 + y, 1/2 - z. ^e x, 1 + y, z. ^f x, 5/2 - y, -1/2 + z.

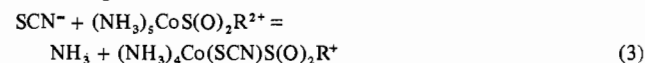
0.054 (12) Å. In $[(\text{NH}_3)_5\text{CoSO}_3]^+$ the comparable data are as follows: average cis Co-N = 1.966 (2) Å; trans Co-N = 2.055 (2) Å; STE = 0.089 (3) Å.

Only weak hydrogen bonds (see Tables X and XI) are present in these structures, and they cannot be correlated with Co-N distances. For example, in $[(\text{NH}_3)_5\text{CoSO}_3]^+$ N(4) participates in no hydrogen bonds, yet it forms the longest of the cis Co-N bonds. In $[(\text{NH}_3)_5\text{CoSO}_3]\text{Cl} \cdot \text{H}_2\text{O}$ the predominant hydrogen bonds are formed between the sulfito oxygen atoms and the ammonia protons from adjacent complex cations, while the chloride anion is hydrogen bonded to the water of hydration rather than to ammonia ligands. In $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ a loose network of hydrogen bonds is formed among the ammonia protons, the oxygen atoms of the perchlorate anions, and the water of hydration.

Ligation Kinetics. Following Halpern,^{4,5} the change in optical density that occurs upon adding SCN^- to an ammoniacal solution of $[(\text{NH}_3)_5\text{CoSO}_3]^+$ is assigned as resulting from approach to the equilibrium



where the *trans*-(NH_3)₄Co(SCN)SO₃ product is formulated by Siebert and Wittke²⁸ as containing N-bonded thiocyanate. By analogy, the optical density change that occurs upon addition of SCN^- to an ammoniacal solution of $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{R}]^{2+}$ is assigned as resulting from approach to the equilibrium



where the product complex $[(\text{NH}_3)_4\text{Co}(\text{SCN})\text{S}(\text{O})_2\text{R}]^+$ undergoes further reaction(s) before complete equilibrium is attained. This assignment is supported by the observation that the rate laws governing approach to equilibria 2 and 3 are of the same form (vide infra). Ion-exchange separation of equilibrated mixtures of SCN^- , NH_3 , and $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_5]^{2+}$ does demonstrate the presence of both 1+ and 2+ charged species, but no information is available as to whether the product $[(\text{NH}_3)_4\text{Co}(\text{SCN})\text{S}(\text{O})_2\text{R}]^+$ complexes contain N-bonded or S-bonded thiocyanate or whether they are of the cis or trans configuration.

For $[(\text{NH}_3)_5\text{CoSO}_3]^+$, $[(\text{NH}_3)_4\text{CoS}(\text{O})_2\text{C}_6\text{H}_5]^{2+}$ and $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$, the rates of approach to the equilibria described in eq 2 and 3 have been determined under the concentration conditions (a) $[\text{NH}_3] = 0.01, 0.05, 0.10,$ and 0.15 M with $[\text{SCN}^-] = 0.50$ M and (b) $[\text{SCN}^-] = 0.01, 0.20, 0.50,$ and 0.99 M with $[\text{NH}_3] = 0.01$ M. At these concentrations, both NH_3 and SCN^- are in pseudo-first-order excess over the cobalt complex concentration (ca. 0.003 M) since the equilibrium quotients governing eq 2 and 3 are < 0.1 (vide infra); in the worst case, concentrations of NH_3 and SCN^- vary

Table XII. Derived Rate and Equilibrium Parameters, in Terms of Eq 4, for Ligation of $[(\text{NH}_3)_5\text{CoSO}_3]^+$, $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_5]^{2+}$, and $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ by SCN^- ^a

| Complex ^b | T, °C | a, s ⁻¹ | b, s ⁻¹ | c | Av % dev ^c | Q ^d |
|----------------------|-------|--------------------------------|----------------------------------|--------------------------------|-----------------------|-----------------|
| 1 | 15 | $(3.4 \pm 3.5) \times 10^{-2}$ | $(3.39 \pm 0.26) \times 10^{-3}$ | 1.2 ± 1.8 | 5.7 | 0.12 ± 0.22 |
| 1 | 25 | $(6.5 \pm 1.8) \times 10^{-2}$ | $(1.03 \pm 0.03) \times 10^{-2}$ | $(5.3 \pm 2.2) \times 10^{-1}$ | 2.2 | 0.09 ± 0.04 |
| 1 | 35 | $(1.2 \pm 0.2) \times 10^{-1}$ | $(2.73 \pm 0.10) \times 10^{-2}$ | $(2.1 \pm 0.7) \times 10^{-1}$ | 4.0 | 0.05 ± 0.02 |
| 2 | 15 | $(5.5 \pm 0.9) \times 10^{-5}$ | $(8.4 \pm 1.8) \times 10^{-6}$ | $(2.2 \pm 1.0) \times 10^{-1}$ | 3.8 | 0.03 ± 0.02 |
| 2 | 25 | $(2.4 \pm 0.7) \times 10^{-4}$ | $(6.6 \pm 0.2) \times 10^{-5}$ | $(3.0 \pm 2.0) \times 10^{-1}$ | 2.8 | 0.08 ± 0.06 |
| 2 | 35 | $(1.2 \pm 0.4) \times 10^{-3}$ | $(2.9 \pm 0.1) \times 10^{-4}$ | $(4.0 \pm 2.4) \times 10^{-1}$ | 4.8 | 0.10 ± 0.07 |
| 3 | 25 | $(5.9 \pm 3.1) \times 10^{-4}$ | $(8.8 \pm 0.2) \times 10^{-5}$ | $(8.4 \pm 6.3) \times 10^{-1}$ | 4.9 | 0.13 ± 0.12 |

^a $k_{\text{obsd}} = (a + bc[\text{SCN}^-]/[\text{NH}_3]) / (1 + c[\text{SCN}^-]/[\text{NH}_3])$; $\mu = 1.00 \text{ M}$ (LiClO_4); $[\text{NH}_3] = [\text{NH}_4^+]$. ^b 1 = $[(\text{NH}_3)_5\text{CoSO}_3]^+$, 2 = $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_5]^{2+}$, 3 = $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$. ^c Average percentage deviation between k_{obsd} and k_{calcd} which is calculated from the optimized a , b , and c parameters listed in this table via eq 4. ^d $Q = bc/a =$ derived equilibrium quotient.

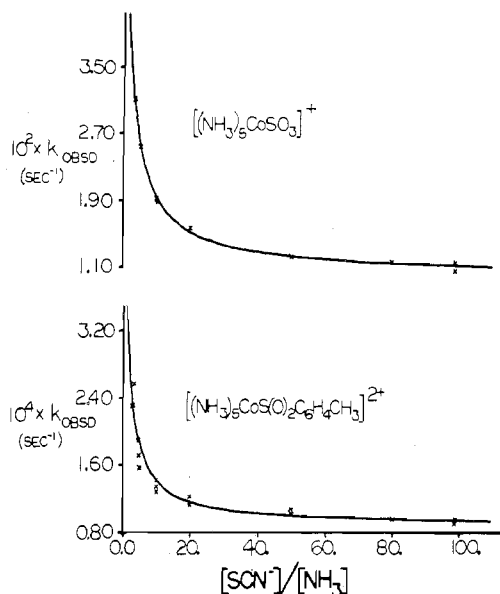


Figure 3. Plots of k_{obsd} vs. $[\text{SCN}^-]/[\text{NH}_3]$ for the ligation of $[(\text{NH}_3)_5\text{CoSO}_3]^+$ (10 points) and $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ (16 points) by SCN^- at 25 °C. Raw data are taken from Tables H²⁶ and J.²⁶ The smooth curves are calculated from eq 4 using the optimized values of a , b , and c listed in Table XII.

by less than 3% during the reaction, and the ratio $[\text{SCN}^-]/[\text{NH}_3]$ varies by less than 6%. Information presented in the Experimental Section suffices to show that under these conditions the rates of approach to equilibria 2 and 3 follow simple first-order kinetics. Tables H–J²⁶ list values of k_{obsd} , the observed first-order rate parameter, at each of the eight concentration conditions specified above, for the sulfito and phenylsulfonato complexes at 15, 25, and 35 °C and for the *p*-toluylsulfonato complex at 25 °C. For all complexes, at all temperatures, the k_{obsd} , $[\text{NH}_3]$, $[\text{SCN}^-]$ data are adequately described by eq 4, the rate law which results from application

$$k_{\text{obsd}} = \frac{a + bc[\text{SCN}^-]/[\text{NH}_3]}{1 + c[\text{SCN}^-]/[\text{NH}_3]} \quad (4)$$

of the limiting $S_{\text{N}}1$ mechanism to the approach to equilibria 2 and 3.^{1,2,4} Table XII lists the optimized values of a , b , and c , as well as the calculated equilibrium quotient $Q = bc/a$, resulting from nonlinear least-squares analysis¹⁵ of the k_{obsd} , $[\text{SCN}^-]/[\text{NH}_3]$ data of Tables H–J.²⁶ Figure 3 shows plots of k_{obsd} vs. $[\text{SCN}^-]/[\text{NH}_3]$ for $[(\text{NH}_3)_5\text{CoSO}_3]^+$ and $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ at 25 °C, where the smooth curves are calculated from optimized values of a , b , and c within eq 4. The most important result to be obtained from Figure 3 is that under identical conditions the sulfito complex reacts about 100 times faster than does the sulfonato complex. Nonlinear least-squares analysis¹⁵ of the temperature de-

Table XIII. Derived Activation Parameters, in Terms of Eq 4–7, for Ligation of $[(\text{NH}_3)_5\text{CoSO}_3]^+$ and $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_5]^{2+}$ by SCN^- ^a

| Term | $[(\text{NH}_3)_5\text{CoSO}_3]^+$ ^b | $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_5]^{2+}$ ^c |
|----------------|---|---|
| ΔS_a^* | -30 ± 13 | 21 ± 12 |
| ΔH_a^* | 10 ± 4 | 29 ± 3 |
| ΔS_b^* | -7.7 ± 1.5 | 14 ± 3 |
| ΔH_b^* | 17.9 ± 0.4 | 27.2 ± 0.9 |
| ΔS_c | -55 ± 18 | 21 ± 3 |
| ΔH_c | -16 ± 6 | 7 ± 7 |

^a Conditions as in Table XII. ΔS^* is expressed in eu; ΔH^* in kcal/mol. ^b These parameters are calculated from 43 independent k_{obsd} values; the average percent deviation between k_{obsd} and k_{calcd} , which is calculated from these parameters within eq 4–7, is 4.1%. ^c See footnote b above; 32 data points, average percent deviation 5.9%.

pendence of the k_{obsd} , $[\text{SCN}^-]/[\text{NH}_3]$ data for $[(\text{NH}_3)_5\text{CoSO}_3]^+$ and $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ within eq 4 but with the temperature dependencies of a , b , and c expressed as

$$a = \frac{kT}{h} (e^{-\Delta H_a^*/RT}) (e^{\Delta S_a^*/R}) \quad (5)$$

$$b = \frac{kT}{h} (e^{-\Delta H_b^*/RT}) (e^{\Delta S_b^*/R}) \quad (6)$$

$$c = (e^{-\Delta H_c/RT}) (e^{\Delta S_c/R}) \quad (7)$$

leads to the activation parameters listed in Table XIII.

Palmer^{4,14} has also studied the ligation of $[(\text{NH}_3)_5\text{CoSO}_3]^+$ by SCN^- (eq 2) under similar conditions (25 °C, $\mu = 0.46 \text{ M}$ (NaClO_4), $[\text{NH}_3] = [\text{NH}_4^+]$), and, where comparable, his raw k_{obsd} , $[\text{SCN}^-]/[\text{NH}_3]$ data are in excellent agreement with the data of Table H.²⁶ For example, in two experiments with $[\text{SCN}^-]/[\text{NH}_3] = 10.7$ Palmer¹⁴ obtained $k_{\text{obsd}} = 0.0181$ and 0.0198 s^{-1} , while Table H²⁶ shows for $[\text{SCN}^-]/[\text{NH}_3] = 10.0$ and 25 °C, $k_{\text{obsd}} = 0.0190 \pm 0.0002 \text{ s}^{-1}$. Under the conditions used in both studies it is the parameter b which largely determines k_{obsd} (at high $[\text{SCN}^-]/[\text{NH}_3]$, $k_{\text{obsd}} = b$; see eq 4), and therefore the agreement in raw data is reflected in similar values for the derived parameter b ; Palmer reported $b = 0.012 \pm 0.001 \text{ s}^{-1}$, and from Table XII $b = 0.0106 \pm 0.0003 \text{ s}^{-1}$ (25 °C). However, the parameters a and c of eq 4 are only poorly defined when eq 4 is used with experimentally accessible $[\text{SCN}^-]/[\text{NH}_3]$ values, and the a and c values obtained by Palmer^{4,14} do not agree at all with the values obtained in this work. This is not unexpected since Palmer derived a and c from a linear analysis in which intercept = $1/a$ and slope = c/a ; this analysis provides only a very imprecise estimate of a , very highly correlated values of a and c , and a correspondingly imprecise determination of c . The nonlinear least-squares analysis used in this study¹⁵ is better suited for

obtaining meaningful measures of a and c . From Table XIII, at 25 °C, $a = 0.065 \pm 0.018 \text{ s}^{-1}$ and $c = 0.53 \pm 0.22$, whereas Palmer's values¹⁴ for these parameters are $a = 1.75 \text{ s}^{-1}$ and $c = 26$. However, it should be noted that the value of Palmer's slope = $c/a = 15 \text{ s}$ is much better defined than the value of either a or c alone, and this slope agrees well with our calculated $c/a = 8 \pm 4 \text{ s}$ (25 °C).

Discussion

Synthesis and Characterization. Both the S-bonded sulfito and the S-bonded arylsulfinatopentaamminecobalt(III) complexes may be prepared by simple substitution of the free ligands onto a pentaamminecobalt(III) center. While the sulfito preparation¹² proceeds satisfactorily in water using $[(\text{NH}_3)_5\text{CoOH}_2]^{3+}$ as starting material, the sulfinato preparations give much better yields in Me_2SO using $[(\text{NH}_3)_5\text{Co}(\text{Me}_2\text{SO})]^{3+}$ as starting material (this complex may be prepared beforehand²⁹ or may be generated in situ from $[(\text{NH}_3)_5\text{CoOH}_2]^{3+}$ ³⁰). It is interesting that in both of these reactions the only detectable products contain the S-bonded linkage isomers, even though the O-bonded isomers would be predicted³¹ to be more stable on the basis of "hard-soft" considerations.³² Contrariwise, only the O-bonded isomers result from the reaction of $[(\text{NH}_3)_5\text{CoOH}_2]^{3+}$ with SeO_3^{2-} ³³ and the reaction of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ with SO_3^{2-} .³⁴ The reasons for these differences are undoubtedly kinetic in origin but have not yet been elucidated.

Since the trans ammonia ligand of both the sulfito and sulfinato complexes is labile (vide infra), the presence of excess free NH_3 is required to maintain the pentaamminecobalt(III) moiety in solution. Therefore, recrystallizations and determinations of visible-UV spectra have been conducted in aqueous NH_3 solutions. The ¹H NMR spectra (Table I) of the arylsulfinato complexes determined in $\text{Me}_2\text{SO}-d_6$ regularly show a trans NH_3 peak that integrates to less than three hydrogen atoms and often show two peaks resulting from the "trans" NH_3 . These observations presumably result from partial replacement of the labile trans NH_3 by $\text{Me}_2\text{SO}-d_6$ giving rise to two peaks—one from the residual trans NH_3 and one from the displaced NH_3 (this latter peak is often obscured).

The infrared spectrum of anhydrous $[(\text{NH}_3)_5\text{CoSO}_3]\text{Cl}$ has been reported by Newman and Powell,³⁵ who assigned the band at 1110 cm^{-1} as the asymmetric SO_3 stretch ν_3 and that at 985 cm^{-1} as the symmetric SO_3 stretch ν_1 . The presence of two strong bands of equal intensity at 994 and 982 cm^{-1} in the infrared spectrum of the hydrated crystal (Table I) shows that this assignment is in fact inverted. In $[(\text{NH}_3)_5\text{CoSO}_3]\text{Cl}\cdot\text{H}_2\text{O}$, interaction of the individual oxygen atoms of the SO_3^{2-} ligand with the coordinated ammonia molecules (vide infra) lowers the site symmetry of SO_3^{2-} from C_{3v} . This in turn causes splitting of ν_3 . The band at 1105 cm^{-1} is therefore assigned as ν_1 and as expected,³⁵ relative to free SO_3^{2-} ($\nu_1 = 1000 \text{ cm}^{-1}$, $\nu_3 = 950 \text{ cm}^{-1}$ ³⁶), ν_1 and ν_3 of coordinated SO_3^{2-} have been raised in energy by ca. 100 and 40 cm^{-1} , respectively.

The structural and chemical similarities of the compounds listed in Table I allow the energies of the observed visible-UV peaks to be quantitatively related. For the sulfinato complexes, $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{Ar}]^{2+}$ and $[(\text{en})_2\text{CoS}(\text{O})_2\text{CH}_2\text{CH}_2\text{NH}_2]^{2+}$, these relations are shown diagrammatically in Figure 4. The assumptions used to construct Figure 4 are that (a) the ligand field splitting of the d orbitals may be treated within an octahedral approximation, (b) the energy of the sulfur orbital from which the LTMCT originates is independent of whether an alkyl or aryl group is bonded to sulfur, and (c) the energy of the t_{2g} orbitals is independent of whether the ancillary ligands are NH_3 or en and also independent of whether an alkyl or aryl group is bonded to sulfur. Given these as-

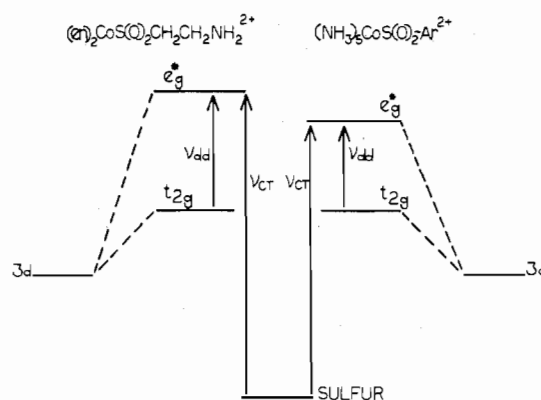


Figure 4. Schematic representation of observed electronic transitions for $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{Ar}]^{2+}$ and $[(\text{en})_2\text{CoS}(\text{O})_2\text{CH}_2\text{CH}_2\text{NH}_2]^{2+}$. Energy levels are not drawn to scale.

sumptions it is seen that the difference in energies of the d-orbitals transitions (ν_{dd}) for the en and NH_3 complexes will be equal to the difference in energies of the LTMCT transitions (ν_{CT}) for the en and NH_3 complexes. Thus $\nu_{dd}(\text{en}) - \nu_{dd}(\text{NH}_3) \approx 1600 \text{ cm}^{-1}$ which is equivalent to $\nu_{CT}(\text{en}) - \nu_{CT}(\text{NH}_3) \approx 1700 \text{ cm}^{-1}$. This energy difference represents the additional destabilization of the e_g^* orbitals by the stronger field en ligands.³⁷ In addition, the difference in energy between ν_{dd} and ν_{CT} for the same compound gives an estimate of the energy gap between the t_{2g} orbitals and the sulfur orbital from which the LTMCT originates. For $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{Ar}]^{2+}$ this difference is ca. 11450 cm^{-1} which is equivalent to the ca. 11550 cm^{-1} observed for $[(\text{en})_2\text{CoS}(\text{O})_2\text{CH}_2\text{CH}_2\text{NH}_2]^{2+}$.

The energies of the e_g^* and t_{2g} orbitals in $[(\text{NH}_3)_5\text{CoSO}_3]^{+}$ are not expected to be drastically shifted from the energies of the comparable orbitals in $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{Ar}]^{2+}$. Therefore, the greater energy of the LTMCT band in the sulfito complex, $\nu_{CT}(\text{SO}_3^{2-}) - \nu_{CT}(\text{ArSO}_2^-) \approx 2900 \text{ cm}^{-1}$, may be ascribed to the fact that the sulfur orbital from which this transition originates is ca. 2900 cm^{-1} more stable in SO_3^{2-} than in ArSO_2^- .

Structural Characteristics of $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$. Coordination of the sulfur atom of the *p*-toluenesulfinate anion to the pentaamminecobalt(III) center induces a structural trans effect (STE) of $0.054(12) \text{ \AA}$. One of the cis Co-N bonds (Co-N(3), $1.986(3) \text{ \AA}$) appears somewhat longer than the other three ($1.960(4)$, $1.963(4)$, $1.966(3) \text{ \AA}$). While the presence of strong hydrogen bonding has previously been invoked³⁸ to explain such a lengthened cis Co-N bond, this explanation seems unlikely here; the listing of possible hydrogen bonds in Table X shows that the hydrogen bonds formed by the N(3) ammonia are very similar to those formed by the other cis ammonia ligands. We believe it is much more likely that the apparent lengthening of the Co-N(3) bond is due to our inability to correctly position the hydrogen atoms around N(3), resulting in a compensatory motion of N(3) toward the electron density of these hydrogen atoms. To probe this hypothesis, we refined a model with anisotropic thermal parameters for all nonhydrogen atoms, but with all ammine hydrogen atoms removed. After convergence, the Co-N(3) bond shortened slightly to $1.981(6) \text{ \AA}$ and the other cis Co-N bonds lengthened to $1.974(5)$, $1.976(4)$, and $1.981(6) \text{ \AA}$, giving an average cis Co-N distance of $1.978(4) \text{ \AA}$. That is, without hydrogen atoms in the model, the Co-N(3) distance is not "anomalously" lengthened. Since the trans Co-N distance in this model with no ammine hydrogen atoms also lengthens ($2.035(4) \text{ \AA}$), the trans effect calculated here ($0.057(6) \text{ \AA}$) is essentially the same as that calculated for the model containing ammine hydrogen atoms. Thus, although we find no evidence from difference maps, etc.,

which would lead us to reposition the hydrogen atoms about N(3), it appears that the hypothesized misassignment of ammine hydrogen atom density adequately accounts for the differing cis Co-N bond lengths. It is clear that small differences in Co-N bond lengths (0.01–0.02 Å) must be treated with extreme caution even if the estimated standard deviations on the Co-N bond lengths are very small.

We have now determined the structures of three sulfinato-cobalt(III) complexes and the associated STE's. The 0.054 (12) Å STE reported here for $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ is in good agreement with the 0.049 (5) Å reported¹⁰ for $[(\text{en})_2\text{CoS}(\text{O})_2\text{CH}_2\text{CH}_2\text{NH}_2]^{2+}$ and the 0.060 (6) Å observed³⁹ for $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_5]^{2+}$. These three independent values may be used to compute 0.054 (6) Å as the best estimate of the sulfinato-induced STE.

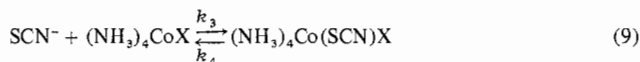
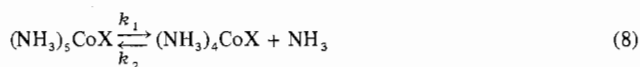
Distortions from the ideal 90° bond angles of octahedral geometry about cobalt may be ascribed primarily to steric interaction between the toluyl ring and the N(5) cis ammonia ligand. The S-C(1) bond of the sulfinate ligand is in an eclipsed configuration with respect to the Co-N(5) bond. The C(1)-N(5) distance of 3.120 (6) Å is much less than the contact distance (3.6 Å) predicted using 1.7 Å for the half-thickness of the aromatic ring and 1.9 Å for the van der Waals radius of the ammonia ligand.⁴⁰ This minimal C(1)-N(5) distance of 3.12 Å has been generated by opening the N(5)-Co-S angle to 94.2 (1)° and opening the Co-S-C(1) angle to 112.9°. Torsional motion of the toluene moiety about the Co-S bond is evident from inspection of Figure 1; the maximum root-mean-square displacements of C(3-7) lie in the plane of the aromatic ring and are directed perpendicular to the S-C(1) bond.

The oxygen atoms of the perchlorate anions show the usual large root-mean-square displacements due to librational motion and/or disorder. One oxygen atom of each anion, O(83) and O(92), has smaller displacements than the others, and inspection of Table X shows that these two atoms are involved in stronger hydrogen bonds than are any of the other perchlorate oxygen atoms. The Cl-O(83) and Cl-O(92) distances (1.449 (5) and 1.445 (6) Å, respectively) are considerably greater than the average Cl-O distance (1.408 (11) Å; computed without O(83) and O(92)). The apparent shortening of a bond, one end of which is undergoing relatively large excursions perpendicular to the bond axis, is merely an artifact of the particular treatment of anisotropic thermal motion used in the least-squares calculation.

Structural Characteristics of $[(\text{NH}_3)_5\text{CoSO}_3]\text{Cl}\cdot\text{H}_2\text{O}$. Other than the striking STE of 0.089 (3) Å, this structure is quite as expected. Steric crowding between O(1) of the sulfite and the N(1) cis ammonia ligand causes the N(1)-Co-S angle to open to 93.1 (1)°, a somewhat smaller distortion than the 94.2 (1)° caused by the larger toluyl group in $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ (vide supra). The S-O bonds average 1.483 (4) Å, somewhat shorter than that observed in the uncomplexed ion (1.504 (3) Å).⁴¹ Similar shortening of S-O bond lengths on complexation occurs in $[(\text{en})_2\text{Co}(\text{SO}_3)(\text{NCS})]$, 1.485 (2) Å,⁴² $[(\text{en})_2\text{Co}(\text{SO}_3)(\text{H}_2\text{O})]^+$, 1.452 (4) Å,⁴³ and $[(\text{quaterpyridyl})\text{Co}(\text{SO}_3)(\text{H}_2\text{O})]^+$, 1.456 (4) Å,⁴⁴ and this phenomenon has been reviewed.^{45,46}

Kinetic Trans Effect. Under the conditions of our studies, thiocyanate does not displace ammonia from hexamminecobalt(III) at a detectable rate whereas it does displace ammonia from $[(\text{NH}_3)_5\text{CoSO}_3]^+$ and $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{R}]^{2+}$ on time scales of minutes and hours, respectively. Therefore both S-bonded sulfite and sulfinate ligands induce a marked lability in the pentaamminecobalt(III) center. The labilized ligand in the sulfite complex is known⁴⁵ to be the trans NH_3 , and this is assumed to also be the case in the sulfinate complexes. Of the mechanisms consistent with the form of

the rate law (eq 4) governing labilized ligation by SCN^- , only the $\text{S}_{\text{N}}1$ limiting mechanism and the prior association mechanism are chemically plausible.^{1,2} A large body of evidence compiled by us^{1,2} and others³⁻⁸ strongly indicates that these labilized cobalt(III) substitution reactions proceed by the $\text{S}_{\text{N}}1$ limiting mechanism,⁴⁷ and an indirect argument presented below supports this conclusion. Therefore all further discussion will be couched in terms of this mechanism; the reactions to be considered are



where X = SO_3^{2-} or RSO_2^- . Assuming a steady state for $(\text{NH}_3)_4\text{CoX}$ leads to

$$k_{\text{obsd}} = \frac{k_4 + (k_1k_3/k_2)[\text{SCN}^-]/[\text{NH}_3]}{1 + (k_3/k_2)[\text{SCN}^-]/[\text{NH}_3]} \quad (10)$$

where from eq 4 $a = k_4$, $b = k_1$, $c = k_3/k_2$, and the equilibrium quotient $Q = k_1k_3/k_2k_4 = bc/a$.

Within the limiting $\text{S}_{\text{N}}1$ formalism the rate parameters k_1 and k_4 describe dissociative cleavage of bonds trans to sulfur and therefore provide a direct measure of the kinetic trans effect (KTE) induced by coordinated sulfur.² From the data of Table XII the ratio $k_1^{\text{SO}_3^{2-}}/k_1^{\text{RSO}_2^-}$ at 25 °C is calculated to be 160 ± 7 for R = C_6H_5 and 120 ± 4 for R = $\text{C}_6\text{H}_4\text{CH}_3$, while the ratio $k_4^{\text{SO}_3^{2-}}/k_4^{\text{RSO}_2^-}$ is calculated to be 270 ± 40 for R = C_6H_5 and 110 ± 40 for R = $\text{C}_6\text{H}_4\text{CH}_3$. These several values of the relative KTE exerted by sulfite and sulfinate sulfur are in good agreement with each other and also with an independently determined value from a markedly different system. For the $\text{S}_{\text{N}}1$ ligation of trans sulfite- and *p*-toluenesulfinate-methanolbis(dimethylglyoximate)cobalt(III) complexes by thiourea in methanol at 25 °C, $k_1^{\text{SO}_3^{2-}}/k_1^{\text{RSO}_2^-} = 111 \pm 7$. Thus, at 25 °C SO_3^{2-} effects a KTE that is more than 2 orders of magnitude greater than that effected by RSO_2^- . Moreover, from the various systems studied it is seen that the relative abilities of SO_3^{2-} and RSO_2^- to promote trans labilization in cobalt(III) are essentially independent of the nature of the leaving ligand, entering ligand, cis ligand, solvent, formal charges, etc. This result is readily explicable within the limiting $\text{S}_{\text{N}}1$ formalism; i.e., the relative rates of dissociative bond cleavage are primarily dependent upon the nature of the trans ligand. However, the explanation of this result within the prior association mechanism would require an unrealistically fortuitous cancelation of several factors.

The data of Table XII also show that values of k_3/k_2 ($=c$, the competition ratio) and Q ($=bc/a$, the equilibrium quotient) are similar for the SO_3^{2-} and RSO_2^- systems. This result implies that, at least at the high ionic strength used in this study, the formal charge on the cobalt complex is not important in determining these parameters and reemphasizes the difficulty of interpreting trans effects from competition ratios.¹ Furthermore, in combination with the consistent rate ratios described above these similar k_3/k_2 and Q values provide support for our contention that the $[(\text{NH}_3)_5\text{CoSO}_3]^+$ and $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{R}]^{2+}$ ligation systems are analogous except for the extent of the KTE.

The temperature-dependence data of Table XIII show that the greater KTE induced by SO_3^{2-} , relative to RSO_2^- , results entirely from the smaller enthalpy of activation required for dissociation of the ligand trans to SO_3^{2-} . Thus, the difference in activation enthalpies, $\Delta H^*(\text{RSO}_2^-) - \Delta H^*(\text{SO}_3^{2-})$, is 9.3 ± 1.0 kcal/mol for k_1 ($=b$, corresponding to dissociative cleavage of the Co-NH₃ bond) and 19 ± 5 kcal/mol for k_4 ($=a$, corresponding to dissociative cleavage of the Co-NCS bond).

However, this ΔH^* effect is partially offset by the ΔS^* terms which favor substitution trans to RSO_2^- ; thus, the differences in activation entropies, $\Delta S^*(\text{RSO}_2^-) - \Delta S^*(\text{SO}_3^{2-})$, are 21 ± 3 eu for k_1 and 50 ± 20 eu for k_4 . Following arguments first presented by Tobe,⁴⁸ these differences in ΔS^* values are taken to imply that the five-coordinate $\text{S}_{\text{N}}1$ intermediates have different geometries, the low-entropy sulfito intermediate approximating a tetragonal pyramid (minimal rearrangement takes place upon ligand dissociation) and the high-entropy sulfinato intermediate approximating a trigonal bipyramid. This interpretation is consistent with the greater steric requirements of RSO_2^- over SO_3^{2-} which may be better accommodated within the trigonal-bipyramidal geometry. The greater steric requirements of RSO_2^- over SO_3^{2-} are readily apparent from the ground-state crystal structures of $[(\text{NH}_3)_5\text{CoSO}_3]^+$ and $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3]^{2+}$ described above. A similar relation between ΔS^* and the size of the trans group has previously been noted by Tobe,⁴⁹ who reported that for aquation of chloride from *trans*- $[(\text{en})_2\text{Co}(\text{Cl})\text{OOCR}]^+$, ΔS^* is more positive when R is the larger phenyl group ($\Delta S^* = 13.2 \pm 2.2$ eu) than when R is methyl ($\Delta S^* = 6.7 \pm 0.8$ eu).

Interrelations between Kinetic and Structural Trans Effects.

A correlation between the extent of the structural trans effect (STE) exerted by a ligand X and the ability of X to labilize the ligand situated trans to it (KTE) is expected on the basis that a longer metal-ligand bond is a weaker bond which is therefore cleaved more readily in either a dissociative or associative process.⁵⁰ This expected correlation is directly established in a qualitative sense by the data presented in this paper: the STE induced by SO_3^{2-} on NH_3 is 0.035 (7) Å larger than that induced by RSO_2^- ; the KTE induced by SO_3^{2-} on NH_3 is 160 ± 7 times that induced by RSO_2^- , this effect originating in a markedly smaller ΔH^* for the sulfito reaction ($\Delta H^*(\text{RSO}_2^-) - \Delta H^*(\text{SO}_3^{2-}) = 9 \pm 1$ kcal/mol). While these data are insufficient to allow a direct, quantitative evaluation of the correlation between STE's and KTE's, they do suffice to permit discussion of three possible interrelations between these phenomena.

(1) Stynes and Ibers⁵¹ have deduced from the crystal structures of several Fe^{II} , Fe^{III} , Ru^{II} and Ru^{III} complexes that changing the charge on the central metal atom from 3+ to 2+ leads to a 0.04-Å lengthening of the metal-ligand bonds; this lengthening is equivalent in magnitude to the difference in STE's observed in this work (0.035 (7) Å). It is generally accepted^{52,53} that in substitution reactions of cobalt(III) complexes, a decrease in the formal charge of the complex by 1 unit causes a 10^2 - 10^3 increase in the rate of substitution; this increase in rate is equivalent in magnitude to the increase in KTE observed in this work (160 ± 7). Thus, on solely a phenomenological (bond length and rate of dissociation) basis, the ammonia ligand trans to SO_3^{2-} behaves as though it experiences an approximately 1 unit lower central-metal charge than does the ammonia ligand trans to RSO_2^- . In terms of bond lengths this is a phenomenon specific to the trans ligand since the average cis Co-N bond lengths of the two complexes are equal within experimental error (1.969 (12) and 1.966 (2) Å for the RSO_2^- and SO_3^{2-} complexes, respectively). An equivalent statement cannot be made for the rates of dissociation since there are no data available on the kinetics of substitution of the cis ligands.

(2) Considerable success has been achieved⁵⁴ in correlating the rates of substitution reactions of cobalt(III) complexes with the energy of the first ligand field spectral band—the lower the energy of this band, the lower the ligand field contribution to the activation energy (LFAE) and the faster the rate of substitution. In the pentaamminecobalt(III) complexes studied herein, the SO_3^{2-} complex has a stronger ligand field (by ca.

300–400 cm^{-1}) than does the RSO_2^- complex; however the sulfito complex is more than 2 orders of magnitude more labile than the sulfinato complex. It is therefore clear that LFAE is *not* a predominant factor in determining the KTE.

(3) By using a simple harmonic oscillator model⁵⁵ and assuming that the different ΔH^* values governing the KTE arise from the different energies necessary to stretch the trans Co-N bonds from their ground-state distances R to some common transition-state distance R^* , we can calculate a value of R^* .

$$\Delta H^*(\text{RSO}_2^-) - \Delta H^*(\text{SO}_3^{2-}) = k' [(R^* - R(\text{RSO}_2^-))^2 - (R^* - R(\text{SO}_3^{2-}))^2] \quad (11)$$

Using the difference in ΔH^* of 9 kcal/mol, $R(\text{RSO}_2^-) = 2.023$ Å, $R(\text{SO}_3^{2-}) = 2.055$ Å, and a value of k' derived from a force constant^{51,56} $k = 1.7 \times 10^5$ dyn/cm for both Co-NH₃ bonds, R^* is calculated to be 3.2 Å. This value is in excellent agreement with the 3.0–3.2 Å distance calculated by Stranks⁵⁷ as the distance to which a Co-O bond must be stretched in order to attain the transition state for ligand substitution. Since Stranks' estimate of R^* is obtained from volume of activation measurements on the oxalate-aquo ligand interchange of $[(\text{en})_2\text{Co}(\text{OH}_2)_2]^{3+}$, it does not depend on the harmonic oscillator model or on any of the assumptions inherent in our calculation. The excellent agreement between these two distinctly derived R^* estimates encourages us to use the value $R^* = 3.2$ Å, along with the above harmonic oscillator model and a ground-state Co-N distance of 1.966 Å, to estimate the enthalpy of activation for NH₃ dissociation from $[(\text{NH}_3)_6\text{Co}]^{3+}$ as 44 kcal/mol. While this number has not yet been experimentally determined, our estimate is consistent with the known^{58,59} very slow rate of ammonia exchange between $[(\text{NH}_3)_6\text{Co}]^{3+}$ and free ammonia. In addition, it should be noted that the simple harmonic oscillator model used above predicts that for small changes in ground-state Co-N bond distances R , differences in activation enthalpies will depend linearly upon differences in R . Thus

$$\Delta H_a^* - \Delta H_b^* = k(R_a - R_b)(R^* - \bar{R}) \quad (12)$$

where $\bar{R} = (R_a + R_b)/2$ and the quantity $(R^* - \bar{R})$ is constant when changes in \bar{R} are small compared to R^* . Experiments designed to test this prediction are being undertaken.

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Registry No. $[(\text{NH}_3)_5\text{CoSO}_3]\text{Cl} \cdot \text{H}_2\text{O}$, 52242-27-0; $(\text{NH}_3)_5\text{CoSO}_3^+$, 53108-45-5; $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, 64715-13-5; $(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_4\text{CH}_3^{2+}$, 64715-11-3; $[(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_5](\text{ClO}_4)_2$, 64715-10-2; $(\text{NH}_3)_5\text{CoS}(\text{O})_2\text{C}_6\text{H}_5^{2+}$, 64715-09-9; aquopentaamminecobalt(III) perchlorate, 14403-82-8; SCN^- , 302-04-5.

Supplementary Material Available: Tables A–J listing observed and calculated structure factors, anisotropic thermal parameters for nonhydrogen atoms, hydrogen atom positional parameters, refined bond lengths and bond angles involving hydrogen atoms, and observed rate constants as a function of $[\text{NH}_3]$, $[\text{SCN}^-]$, and temperature (26 pages). Ordering information is given on any current masthead page.

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- (56) $k' = 122.4$ (kcal/mol)/(Å/bond)². The calculated value of R^* is only slightly dependent on the choice of k ; with $k = 1.5 \times 10^5$ dyn/cm, $R^* = 3.34$ Å.
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Oxidative Decarboxylation of Glycylglycyl-L-histidine by Copper(II) Hydroxide: X-Ray Structural Characterization of α,β -Didehydroglycylglycylhistaminatocopper(II) Dihydrate

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Red crystals of the title complex were obtained by the reaction of copper(II) hydroxide with glycylglycyl-L-histidine in water (ratio of metal:ligand 1:1). The structure of this complex, $C_9H_{11}O_2N_5Cu \cdot 2H_2O$, has been determined from three-dimensional x-ray counter data by Patterson and Fourier methods. The compound crystallizes in the triclinic space group $P\bar{1}$, with two formula units per cell. The cell constants are $a = 7.315$ (2) Å, $b = 10.110$ (3) Å, $c = 9.609$ (3) Å, $\alpha = 71.59$ (3)°, $\beta = 86.66$ (2)°, and $\gamma = 110.74$ (2)°. Full-matrix least-squares refinement using 1636 independent reflections has reached $R = 0.038$. The central copper(II) atom is square planar, coordinating to four nitrogen atoms of the ligand. The metal does not show any weak interaction (less than 3.0 Å) with any fifth or sixth donor atom. The distances Cu-N(amino), Cu-N(peptide 1), Cu-N(peptide 2), and Cu-N(imidazole) are 2.028 (4), 1.898 (3), 1.960 (3), and 1.941 (3) Å, respectively. The two trans N-Cu-N angles are 165.9 (1) and 177.0 (1)°. The shortest separation between copper atoms in neighboring molecules is 3.946 Å. The major feature of the structure is that the original ligand has undergone an oxidative decarboxylation. The C α atom of the histidine residue has lost its carboxylate group and the observed C α -C β distance of 1.340 (6) Å, much shorter than the value of 1.536 (3) Å in histidine, is consistent with a formal double bond between these atoms. All other distances in the ligand are normal. The two water molecules, while not involved in the copper coordination sphere, participate in several hydrogen bonds.

Introduction

Since the tripeptide glycylglycyl-L-histidine (glyglyhis) contains the same potential metal binding sites as the terminal portion of serum albumin,¹⁻³ there has been an enormous amount of recent chemical research on the interactions of copper(II) ions with this tripeptide.⁴⁻⁷ A recent crystallographic study of the *N*-methylamide derivative of the complex confirmed the earlier postulate⁴ that the complex has a

square-planar structure with the copper atom coordinated to four nitrogen atoms of the tripeptide.⁷ In reacting the tripeptide with freshly prepared copper(II) hydroxide, we obtained excellent crystals of what we initially assumed to be the parent complex, Cu(glyglyhis). Upon crystallographic examination, however, we discovered that the tripeptide had undergone decarboxylation, but that the complex retained the square-planar geometry at copper.⁸ The results of our