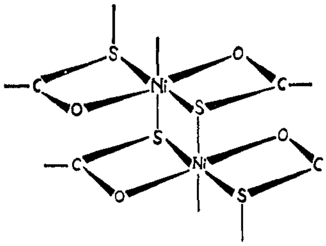
explains the strong oxygen coordination in the Cr(III) complex, the nearly symmetric chelation in Ni(II) and Zn(II) complexes, and the strong sulfur bonding in Cd(II), Hg(II), Cu(I), and Ag(I) complexes.

Electronic Spectra and Probable Configurations of the Complexes.—The electronic spectral data together with their probable assignments for Cr(III) and Ni(II) complexes are given in Table IV. The Cr(III) complex gives two broad d–d transitions centered at 22,980 and 16,260 cm^{-1}. The broadening of these bands suggests a composite nature of the transitions concomitant with the lowering of the octahedral symmetry. The third d–d band, $^4A_2 \rightarrow {}^4T_1(P)$, expected around 37,000 cm^{-1} seems to have merged with the strong $\pi \rightarrow \pi^*$ transition at 38,170 cm^{-1}.

The electronic spectral data together with the paramagnetic moment of 3.31 BM suggests a distorted octahedral configuration around Ni(II). Such a configuration can be satisfied by proposing the polymeric structure



The polymeric nature of the complex could not be substantiated further from molecular weight measurements, because of its insolubility or poor solubility in any suitable solvent. However, a suspension of the complex in petroleum ether (bp 40–50°), when treated with pyridine, yielded green crystals of a complex having the molecular formula $Ni(MTB)_2(py)_2$. The complex is monomeric, with a distorted octahedral symmetry as revealed by the d–d transitions and the magnetic moment. The formation of this complex from $[Ni(MTB)_2]_n$ can be explained by the rupture of the two weaker axial Ni–S bonds by the coordination of two pyridine molecules in their position. The Zn(II) and the Cd(II) complexes may also have the same type of distorted octahedral structure as that of the Ni(II) complex. However, the axial bonds in these complexes appear to be stronger as they are not affected by pyridine.

In the mercury(II) thiobenzoate complex, Hg(II) may be diagonally coordinated with the sulfur atoms from a pair of thiobenzoate groups and possibly also axially to an already coordinated thiobenzoate, thus conferring polymeric nature on the complex. Cu(I) and Ag(I) complexes may have polymeric chains, sulfur of thiobenzoate acting as a bridge between two metal ions. The present data are insufficient to assign an exact coordination to Hg(II), Cu(I), and Ag(I).

Acknowledgment.—The authors wish to thank Professor M. R. A. Rao, for his interest in the work, and Evans Chemetics, New York, N. Y., for the gift sample of thiobenzoic acid.

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Dissociative Mechanisms for Substitution of Sulfito Complexes

BY D. R. STRANKS AND J. K. YANDELL

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Above pH 12, the substitution of *trans*-$Co(en)_2SO_3OH$ by SO_3^{2-} to form *trans*-$Co(en)_2(SO_3)_2^-$ is reversible with an equilibrium constant $K_I = 0.36_8$ at 25° and $\Delta H_I = 0.25 \pm 0.2$ kcal mol^{-1}. The rate law for sulfite substitution is consistent with a reversible two-step limiting SN1 mechanism. The rate parameters for formation of the intermediate $Co(en)_2SO_3{}^+$ from *trans*-$Co(en)_2(SO_3)_2^-$ are $k(25°) = 0.11_1$ sec^{-1}, $\Delta H^{\ddagger} = 20.5 \pm 0.6$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 5.9 \pm 3$ eu while formation of the same intermediate from *trans*-$Co(en)_2SO_3OH$ is described by $k(25°) \geq 3$ sec^{-1}, $\Delta H^{\ddagger} = 21 \pm 2$ kcal mol^{-1}, and $\Delta S^{\ddagger} \geq 4$ eu. Hydroxide ion is at least 50 times more reactive than sulfite ion toward $Co(en)_2SO_3^+$. At pH 8.1, substitution of *trans*-$Co(en)_2SO_3OH_2^+$ by SO_3^{2-} is virtually complete and the observed rate law is consistent with a limiting SN1 mechanism. The intermediate $Co(en)_2SO_3^+$ is formed from *trans*-$Co(en)_2SO_3OH_2^+$ with $k(25°) = 13.4$ sec^{-1}, $\Delta H^{\ddagger} = 15.9 \pm 0.5$ kcal mol^{-1}, and $\Delta S^{+} = 0.2 \pm 2$ eu. Both N_3^- and HSO_3^- exhibit the same limiting rate for substitution as does SO_3^{2-}. The relative reactivity of sulfite and water (k_s/k_w) toward $Co(en)_2SO_3^+$ is $(9 \pm 5) \times 10^3$. The labilizing effect of the sulfito ligand arises from the unusually low $\Delta H^{\ddagger}$ values for dissociative release of the ligand *trans* to the sulfito ligand.

Introduction

The rates of substitution reactions of cobalt(III) complexes are accelerated markedly by the presence of a sulfito ligand.[1-3] The reaction half-times of seconds or less observed for these sulfito reactions at 25° are at least 10^3 times shorter than for typical substitution reactions of other diamagnetic cobalt(III) complexes.

In the case of the reactant complexes $Co(NH_3)_5SO_3^+$,

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[1] R. S. Murray, D. R. Stranks, and J. K. Yandell, *Chem. Commun.*, 604 (1969).

[2] J. Halpern, R. A. Palmer, and L. M. Blakely, *J. Am. Chem. Soc.*, **88**, 2877 (1966).

[3] H. G. Tsiang and W. K. Wilmarth, *Inorg. Chem.*, **7**, 2535 (1968); P. H. Tewari, R. H. Gaver, H. K. Wilcox, and W. K. Wilmarth, *ibid.*, **6**, 611 (1967).

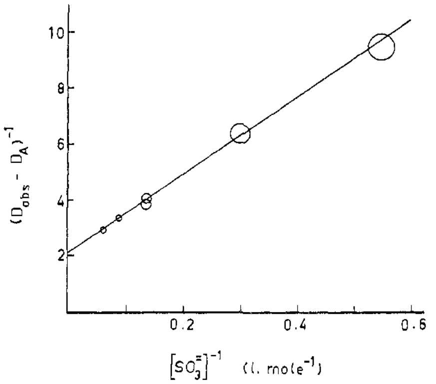

Figure 1.—Determination of K_I and ϵ (eq 3).

$Co(NH_3)_4SO_3OH$, $Co(NH_3)_4SO_3NO_2$, $Co(NH_3)_4SO_3NCS$, and $Co(CN)_4SO_3OH_2{}^{3-}$, substitution proceeds *via* a limiting SN1 or dissociative mechanism which generates an intermediate whose lifetime permits it to discriminate kinetically between different nucleophiles.

The other remarkable property of the sulfito ligand appears to be its ability to direct incoming nucleophiles to the *trans* position in the product complex. This property has been demonstrated most clearly[3a] in substitution reactions of the dimethylglyoxime complex *trans*-$Co(DH)_2SO_3OH_2{}^-$. Whereas this species is substituted by $SO_3{}^{2-}$ *via* a dissociative mechanism, other nucleophiles like thiourea and azide appear to react by an associative mechanism.

The present investigation aimed at gathering further evidence for dissociative substitution reactions of sulfito complexes. A second aim was to evaluate activation parameters for these reactions in an attempt to elucidate the probable causes of the remarkable labilizing property of the sulfito ligand. None of the earlier investigations has considered the effect of temperature on the substitution reactions of sulfito complexes.

Experimental Section

Materials.—*trans*-$Co(en)_2SO_3OH_2 \cdot ClO_4$ was prepared by the method of Baldwin.[4] The yellow-brown crystalline compound gave on vacuum desiccation for 2 days a red-brown compound which analyzed as $Co(en)_2SO_3 \cdot ClO_4$. All solutions were prepared from the complex in this red-brown form which immediately regenerates *trans*-$Co(en)_2SO_3OH_2 \cdot ClO_4$ on dissolving in water. Solutions of the complex were protected from laboratory light to avoid photodecomposition.

Sigma brand tris(hydroxymethyl)methylamine ("Trizma" base) was used to prepare buffer solutions of pH 8.1. All other reagents were AR quality.

All reactant solutions were made up to an ionic strength of 1.0 *M* with sodium perchlorate, including all solutions used for pH titrations.

pH Measurements.—These were made with a Radiometer titrator, Type TTT1, with glass–calomel electrodes standardized against potassium hydrogen phthalate buffer solutions.[5]

Spectral Measurements.—Optical absorbance measurements were made with a Shimadzu QR-50 spectrophotometer provided with thermostated cell compartment facilities.

Kinetic Measurements.—A stopped-flow apparatus similar in design to that of Laurence and Tregloan[6] was used except that it was adapted to employ light absorption to monitor concentration changes. Rate constants were evaluated from enlarged photographs of the oscilloscope traces.

For most experiments, a wavelength of 432 nm was used to monitor the reactions since this corresponds to the maximum absorption of the *trans*-$Co(en)_2(SO_3)_2{}^-$ ion. However it was confirmed that the measured rate constants were not dependent on the wavelength used.

Results

pK_a of *trans*-$Co(en)_2SO_3OH_2{}^+$.—pK_a values were deduced from the customary acid–base titration curves using 1.0 *M* NaOH as the base titrant. The pK_a values were measured in the same media and over the same temperature range as the rate studies. For the equilibrium

$$trans\text{-}Co(en)_2SO_3OH_2{}^+ \rightleftharpoons trans\text{-}Co(en)_2SO_3OH^0 + H_3O^+$$

the pK_a was found to be 9.45 at 25° and 9.60 at 5°.

The *trans*-$Co(en)_2SO_3OH + SO_3{}^{2-}$ Equilibrium.—In solutions exceeding 0.02 *M* OH^-, the species *trans*-$Co(en)_2SO_3OH_2{}^+$ is in negligible concentration and substitution reactions of the species *trans*-$Co(en)_2SO_3OH$ may be studied. Spectrophotometric measurements showed that sulfite substitution of the hydroxosulfito complex is a reversible equilibrium

$$trans\text{-}Co(en)_2SO_3OH + SO_3{}^{2-} \rightleftharpoons trans\text{-}Co(en)_2(SO_3)_2{}^- + OH^- \qquad (I)$$

The extinction coefficient of *trans*-$Co(en)_2SO_3OH$ in 1 *M* sodium perchlorate at 25° was measured independently as $100_5 \pm 1$ at 432 nm. However the extinction coefficient of the bis-sulfito species cannot be measured directly because of the reversible nature of the equilibrium in basic media.

Defining the equilibrium constant for reaction I as

$$K = \frac{[Co(en)_2(SO_3)_2{}^-][OH^-]}{[Co(en)_2SO_3OH][SO_3{}^{2-}]} \qquad (1)$$

then an initial estimate of K was obtained from the relation

$$K_I = \left\{\frac{D'_{obsd} - D'_A}{[SO_3{}^{2-}]'} - \frac{D'_{obsd} - D''_A}{[SO_3{}^{2-}]''}\right\} \Big/ (D' - D'') \qquad (2)$$

where D'_{obsd} and D''_{obsd} are the observed total optical absorbances of two solutions containing $[SO_3{}^{2-}]'$ and $[SO_3{}^{2-}]''$ and a fixed total concentration of cobalt complex, while D_A' and D_A'' are the optical absorbances due to the remaining unsubstituted $Co(en)_2SO_3OH$ complex in these two solutions. This estimated value of K_I was then used to estimate the concentration and, hence, the optical absorbance, due to the unsubstituted complex. The absorbance due to the product *trans*-$Co(en)_2(SO_3)_2{}^-$ could then be calculated, *i.e.*, $D_{obsd} - D_A$. It then follows from (1) that

$$(D_{obsd} - D_A)^{-1} = \epsilon^{-1} + (\epsilon K_I[SO_3{}^{2-}])^{-1} \qquad (3)$$

where ϵ is the molar extinction coefficient of the disulfito product. Figure 1 illustrates a graphical plot of data according to (3). The final accurate values

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[4] S. Baldwin, *J. Chem. Soc.*, 3123 (1961).

[5] L. G. Sillén and A. Martell, Special Publication No. 17, The Chemical Society, London, 1964.

[6] P. A. Tregloan and G. S. Laurence, *J. Sci. Instr.*, **42**, 869 (1965).

for K_I and ϵ were derived from the slopes and intercepts of graphical plots such as Figure 1.

The value of ϵ was found to be 388 ± 9 M^{-1} cm^{-1} at 432 nm. Values of K_I at different temperatures were found to be 0.35_5 (5°), 0.36_8 (25°), and 0.37_5 (40°). The very small temperature dependence of K_I suggests an enthalpy change $\Delta H_I = 0.25 \pm 0.2$ kcal mol^{-1}.

Rate of Substitution of *trans*-Co(en)$_2$SO$_3$OH by SO$_3^{2-}$.—This was studied under pseudo-first-order conditions with both SO_3^{2-} and OH^- concentrations in excess of [Co(en)$_2$SO$_3$OH]. The observed first-order rate constants, k_{obsd}, were evaluated from the slope of the log (optical absorbance) *vs.* time plots. Table I summarizes values of k_{obsd} measured at constant [OH$^-$] but varying [SO$_3^{2-}$] while Table II summarizes values measured at constant [SO$_3^{2-}$] but varying [OH$^-$]. Each value in these tables is the mean of at least five independent rate measurements and the uncertainty quoted (usually ≤3%) is the mean deviation of these results from the mean value.

TABLE I

DEPENDENCE OF RATE OF SUBSTITUTION OF *trans*-Co(en)$_2$SO$_3$OH BY SO$_3^{2-}$ ON SULFITE CONCENTRATION[a]

[SO$_3^{2-}$], M	k_{obsd}, sec^{-1}	[SO$_3^{2-}$], M	k_{obsd}, sec^{-1}
0.0134	0.127 ± 0.017	0.116	0.314 ± 0.004
0.050	0.197 ± 0.006	0.163	0.380 ± 0.014
0.075	0.235 ± 0.007		

[a] Temperature 25°; 1.0 M ionic strength (NaClO$_4$); [OH$^-$] = 0.024 M; [Co(en)$_2$SO$_3$OH] = 0.00122 M.

TABLE II

DEPENDENCE OF RATE OF SUBSTITUTION OF *trans*-Co(en)$_2$SO$_3$OH BY SO$_3^{2-}$ ON HYDROXIDE ION CONCENTRATION[a]

[OH$^-$], M	k_{obsd}, sec^{-1}	[OH$^-$], M	k_{obsd}, sec^{-1}
0.0132	0.412 ± 0.015	0.10	0.152 ± 0.008
0.024	0.240 ± 0.007	0.25	0.122 ± 0.007
0.049	0.175 ± 0.014		

[a] Temperature 25°; 1.0 M ionic strength (NaClO$_4$); [SO$_3^{2-}$] = 0.075 M; [Co(en)$_2$SO$_3$OH] = 0.00122 M.

Figures 2 and 3 show that these data are consistent with the empirical relation

$$k_{obsd} = \frac{k_f[SO_3^{2-}]}{[OH^-]} + k_r \qquad (4)$$

where k_f and k_r represent the rate constants for the forward and reverse rate constants of equilibrium I. Irrespective of the reaction mechanisms, K_I ($= k_f/k_r$) may be evaluated from the values of (slope)[OH$^-$]/(intercept) (Figure 2) and (slope)[SO$_3^{2-}$]/(intercept) (Figure 3). The respective values of K_I at 25° are 0.37 ± 0.05 and 0.42 ± 0.07 which are in satisfactory agreement with the value of 0.37 ± 0.02 deduced from the independent spectrophotometric measurements. The consistency of the rate data is also demonstrated by the deduced values of k_f and k_r. The data from Figure 2 yield $k_f = (4.09 \pm 0.05) \times 10^{-2}$ sec^{-1} and $k_r = 0.111 \pm 0.005$ sec^{-1} while data from Figure 3 yield $k_f = (4.66 \pm 0.7) \times 10^{-2}$ sec^{-1} and $k_r = 0.11 \pm 0.01$ sec^{-1}.

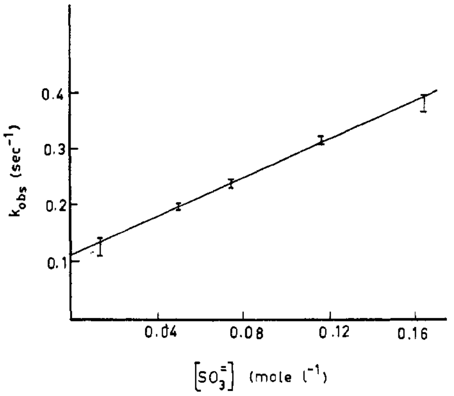

Figure 2.—Dependence of observed rate constant on sulfite concentration at constant [OH$^-$] = 0.024 M.

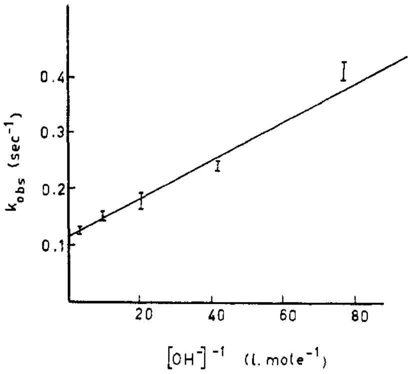

Figure 3.—Dependence of observed rate constant on hydroxide ion concentration at constant [SO$_3^{2-}$] = 0.075 M.

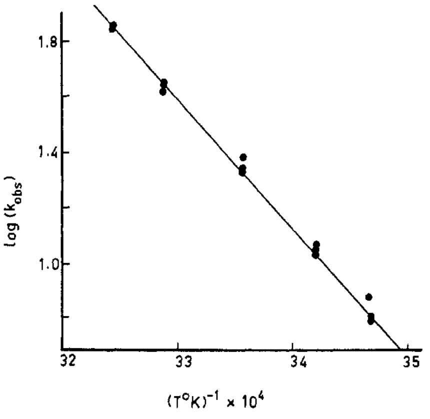

Figure 4.—Temperature dependence of observed rate at [OH$^-$] = 0.024 M and [SO$_3^{2-}$] = 0.075 M.

The temperature variation of k_{obsd}, shown in Figure 4, corresponds to an activation energy of 21.2 ± 0.5 kcal mol^{-1}. Equation 4 shows that this activation energy is a composite quantity. When the independently measured values of K_I and ΔH_I are used to separate k_f and k_r, the activation energy for k_r is 21.3 ± 0.6 kcal mol^{-1} and the activation energy for k_r is 21.1 ± 0.6 kcal mol^{-1}.

Substitution of *trans*-Co(en)$_2$SO$_3$OH$_2^+$ by SO$_3^{2-}$.—A kinetic study of the substitution of the aquosulfito

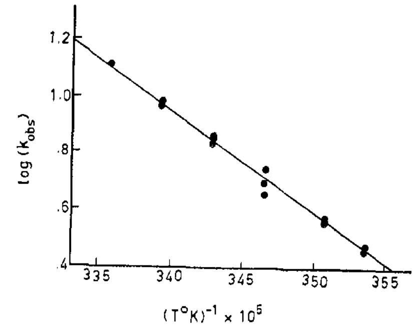

Figure 5.—Temperature dependence of observed rate constant at pH 8.1.

complex was performed at pH 8.1 where 5% of the sulfito complex exists in the hydroxosulfito form. An allowance for the rate contribution from this small amount of hydroxosulfito complex is readily made since the hydroxo complex substitutes some 50 times more slowly than the aquo complex. At pH 8.1, less than 3% of the total sulfite ion exists as HSO_3^- and as bisulfite was shown to substitute at a rate similar to that of sulfite, this concentration of HSO_3^- had a negligible effect on the observed rate.

The substitution reaction was studied under pseudo-first-order conditions with a large excess of sulfite ion. Good first-order kinetic plots were observed under all conditions with half-times ranging from 100 to 20 msec depending on reaction conditions. The 0.1 M "Trizma" base was shown to have no measurable effect on the spectra of the reactants and products and it was assumed that the buffer did not react under the conditions used.

Spectrophotometric measurements revealed that the reaction

$$trans\text{-}Co(en)_2SO_3OH_2^+ + SO_3^{2-} \rightleftharpoons trans\text{-}Co(en)_2(SO_3)_2^- \quad (II)$$

was virtually complete under all the reaction conditions studied. First-order rate constants, k_{obsd}, were measured as a function of $[SO_3^{2-}]$ and the values are summarized in Table III. At high $[SO_3^{2-}]$, k_{obsd} attains a limiting value of 13.4 ± 0.1 sec^{-1} but k_{obsd} is dependent on $[SO_3^{2-}]$ at lower concentrations.

Table III

Dependence of Rate of Substitution of *trans*-$Co(en)_2SO_3OH_2^+$ by SO_3^{2-} on Sulfite Concentration[a]

$[SO_3^{2-}]$, M	k_{obsd}, sec^{-1}	$[SO_3^{2-}]$, M	k_{obsd}, sec^{-1}
0.0166	8.90 ± 0.3	0.075	13.3 ± 0.2
0.033	11.7 ± 0.1	0.117	13.45 ± 0.5
0.065	11.7 ± 0.3	0.158	13.5 ± 0.2

[a] Temperature 25°; 1.0 M ionic strength (Trizma base); pH 8.1; $[Co(en)_2SO_3OH_2^+] = 0.00122\ M$.

Some rate measurements were also conducted in the region of pH 4.1 where less than 1% of the total sulfite exists as SO_3^{2-}. At 22° and an ionic strength of 1.5 M, k_{obsd} = 11.0 sec^{-1}. This value is very similar to the limiting value of k_{obsd} for substitution by SO_3^{2-} observed at a lower ionic strength. Reaction also occurs at pH 2.3, but the substitution rates were not measured under these conditions.

The activation energy for sulfite substitution was evaluated at a constant sulfite concentration of 0.117 M where the limiting rate for sulfite substitution is established. The data are plotted in Figure 5 and correspond to an activation energy of 16.5 ± 0.5 kcal mol^{-1}.

Other Substitution Reactions of *trans*-$Co(en)_2SO_3OH_2^+$.—At pH 8.1, the addition of azide ion to a solution of the aquosulfito complex caused a rapid, marked spectral change which was attributed to the reaction

$$trans\text{-}Co(en)_2SO_3OH_2^+ + N_3^- \rightleftharpoons trans\text{-}Co(en)_2SO_3N_3 + H_2O \quad (III)$$

At $[N_3^-]$ = 0.082 M, 25°, and 1 M ionic strength, a first-order rate constant of 13.6 ± 0.9 sec^{-1} was observed. This is in close agreement with the limiting value of k_{obsd} = 13.9 ± 0.5 observed in a duplicate experiment at high $[SO_3^{2-}]$.

Exchange of solvent $H_2{}^{18}O$ with *trans*-$Co(en)_2SO_3OH_2^+$ at pH 8.1 is complete[1] within the separation time of 2 min at room temperature. Similarly, exchange of $^{35}SO_3^{2-}$ with *trans*-$Co(en)_2(SO_3)_2^-$ is complete within 2 min at room temperature but exchange is incomplete within a separation time of 10 sec.[7]

Substitution Reactions of *cis*-$Co(en)_2(SO_3)_2^-$.—In contrast to *trans*-$Co(en)_2(SO_3)_2^-$, *cis*-$Co(en)_2(SO_3)_2^-$ is not unusually labile with respect to hydrolysis and exchange reactions. For example, aqueous solutions of the *cis* isomer do not hydrolyze measurably over several days at room temperature, nor do these solutions isomerize in the same period, as this would lead to hydrolysis. At pH 8.1, the half-time for hydrolysis of *cis*-$Co(en)_2(SO_3)_2^-$ is at least 10^7 sec, whereas for the *trans* isomer it is 53 msec. The *cis* isomer is subject to acid hydrolysis. At 55° in 2 M $HClO_4$, the half-time for hydrolysis[7] is 12 min; extrapolation to 25° yields a half-time of 840 min. No exchange of $^{35}SO_3^{2-}$ with *cis*-$Co(en)_2(SO_3)_2^-$ could be detected in 10 min at room temperature.[7] Thus it appears that the labilization by sulfito ligands is strongly specific to the position *trans* to the sulfito ligand.

Discussion

Mechanism for *trans*-$Co(en)_2SO_3OH$ Substitution.—The empirical relation (4) representing substitution by SO_3^{2-} of the neutral species *trans*-$Co(en)_2SO_3OH$ involves the unusual reciprocal dependence of rate on hydroxide ion concentration. The following reversible limiting S_N1 mechanism appears to be the only[8] mechanism compatible with the observed rate law

$$trans\text{-}Co(en)_2SO_3H \rightleftharpoons Co(en)_2SO_3^+ + OH^- \quad (IV)$$

$$Co(en)_2SO_3^+ + SO_3^{2-} \rightleftharpoons trans\text{-}Co(en)_2(SO_3)_2^- \quad (V)$$

Assuming that the steady-state approximation is ap-

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[7] Dr. R. S. Murray, private communication; results to be submitted for publication.

[8] Using the known pK_a of the sulfito–aquo complex and its observed rate of substitution, it is readily shown that the alternative substitution of the sulfito–aquo complex makes a negligible contribution to the rate of substitution measured at the high hydroxide ion concentration used.

TABLE IV

ACTIVATION PARAMETERS FOR DISSOCIATION REACTIONS

Reaction	$k(25°)$, sec^{-1}	E_a, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
trans-$Co(en)_2(SO_3)_2^- \rightarrow Co(en)_2SO_3^+ + SO_3^{2-}$	0.111	21.1 ± 0.6	20.5 ± 0.6	5.9 ± 3
trans-$Co(en)_2SO_3OH \rightarrow Co(en)_2SO_3^+ + OH^-$	≥ 3	21.3 ± 2	21 ± 2	≥ 4
trans-$Co(en)_2SO_3OH_2^+ \rightarrow Co(en)_2SO_3^+ + H_2O$	13.0	16.5 ± 0.5	15.9 ± 0.5	0.2 ± 2
trans-$Co(en)_2OHOH_2^{2+} \rightarrow Co(en)OH^{2+} + H_2O$[a]	0.0035[b]	24.0 ± 0.5	23.4 ± 0.5	8.6 ± 3

[a] Mechanism assumed for *trans* ⟷ *cis* isomerization. [b] Reference 10.

plicable to the concentration of the dissociative intermediate $Co(en)_2SO_3^+$, then

$$k_{obsd} = \frac{k_s k_{-OH}[SO_3^{2-}] + k_{OH}k_{-s}[OH^-]}{k_{OH}[OH^-] + k_s[SO_3^{2-}]} \tag{5}$$

where k_{-OH} and k_{OH} are the rate constants for the forward and back reactions of eq IV, and k_s and k_{-s} are the rate constants for the forward and back reactions of eq V. Provided that $k_{OH}[OH^-]$ is much greater than $k_s[SO_3^{2-}]$ over the concentration range employed, then (5) reduces to

$$k_{obsd} = \frac{k_s k_{-OH}[SO_3^{2-}]}{k_{OH}[OH^-]} + k_{-s} \tag{6}$$

which is identical with the form of relation 4. Hence k_f may be equated to the composite term $k_s k_{-OH}/k_{OH} = (4.4 \pm 0.6) \times 10^{-2}$ sec^{-1} at 25° while k_r may be equated to $k_{-s} = 0.111$ sec^{-1}.

The activation energy for k_{-s} is 21.1 kcal mol^{-1} and activation parameters are summarized in Table IV. The activation energy for $k_s k_{-OH}/k_{OH}$ is 21.3 kcal mol^{-1}. The rate constants k_s and k_{OH} refer, respectively, to the competitive substitution by either SO_3^{2-} or OH^- on the "five-coordinate" intermediate $Co(en)_2SO_3^+$. Since this intermediate is expected to be very short lived, both these substitution reactions are expected to be very rapid and their rates may even approach diffusion-controlled rates. It is unlikely therefore that the activation energies will differ by more than 2 kcal mol^{-1}. Consequently the observed activation energy for the term $k_s k_{-OH}/k_{OH}$ is very likely that for the bond-breaking reaction described by k_{-OH}. A value of 21.3 ± 2 kcal mol^{-1} is therefore assigned to k_{-OH} in Table IV.

Equation 6 was derived on the assumption that $k_{OH}[OH^-] \gg k_s[SO_3^{2-}]$. The apparent linearity of the plot of k_{obsd} *vs.* $[SO_3^{2-}]$ enables an approximate limit to be assigned such that $k_{OH} \geq 50k_s$. Using the known value $k_s k_{-OH}/k_{OH} = 4.3 \times 10^{-2}$, this yields in turn a lower limit $k_{-OH} \geq 3$ sec^{-1} corresponding to the reaction

$$\textit{trans}\text{-}Co(en)_2SO_3OH \longrightarrow Co(en)_2SO_3^+ + OH^-$$

This value is assumed in Table IV in calculating the activation parameters for this reaction. A value of 7 sec^{-1} has been reported[8a] for the comparable reaction involving substitution of *trans*-$Co(NH_3)_4SO_3OH$.

The reactions described by k_{-s} and k_{-OH} both involve charge separation in the overall reaction. In both cases, only small positive $\Delta S^{\ddagger}$ values are exhibited suggesting that charge separation is not highly developed in the transition states for formation of the dissociated intermediate $Co(en)_2SO_3^+$.

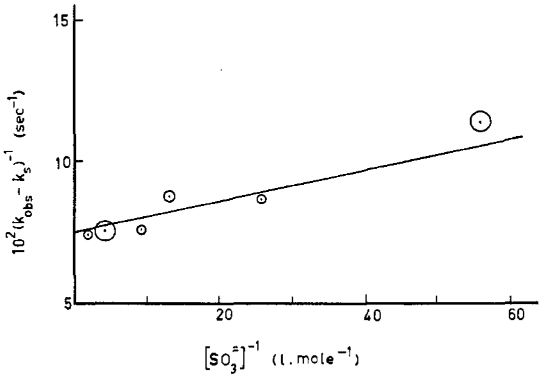


Figure 6.—Dependence of observed rate constant on sulfite concentration at pH 8.1.

Mechanism for *trans*-$Co(en)_2SO_3OH_2^+$ Substitution.—The rate data for substitution of *trans*-$Co(en)_2SO_3OH_2^+$ by SO_3^{2-} are consistent with the following limiting S_N1 mechanism

$$\textit{trans}\text{-}Co(en)_2SO_3OH_2^+ \rightleftharpoons Co(en)_2SO_3^+ + H_2O \tag{VI}$$

$$Co(en)_2SO_3^+ + SO_3^{2-} \rightleftharpoons \textit{trans}\text{-}Co(en)_2(SO_3)_2^- \tag{V}$$

where the forward and reverse reactions of eq VI are described by the rate constants k_{-w} and k_w, respectively, and k_s and k_{-s} for eq V have been defined above. The steady-state approximation for this mechanism leads to

$$k_{obsd} = \frac{k_s[SO_3^{2-}](k_{-w} - k_{-s})\alpha}{k_w[H_2O] + k_s[SO_3^{2-}]} + k_{-s} \tag{7}$$

where $\alpha = (1 + K_a/[H^+])^{-1}$ is a correction term to allow for the small concentration of *trans*-$Co(en)_2SO_3OH$ present as defined by the acidity constant K_a. At pH 8.1, $\alpha = 0.95$. Equation 7 may be rearranged to the form

$$\alpha(k_{obsd} - k_{-s})^{-1} = \frac{k[H_2O]}{k_s[SO_3^{2-}](k_{-w} + k_{-s})} + \frac{1}{(k_{-w} + k_{-s})} \tag{8}$$

Figure 6 shows a graphical plot of the data according to (8) from which $k_{-w} = 13.2 \pm 0.9$ sec^{-1} and $k_w \cdot [H_2O]/k_s = (6 \pm 3) \times 10^{-3}$ at 25°.

The ratio k_s/k_w represents the relative reactivity of the nucleophiles SO_3^{2-} and OH_2 for the intermediate $Co(en)_2SO_3^+$. Assigning $[H_2O] = 55$ *M*, then $k_s/k_w = (9 \pm 5) \times 10^3$. The high relative reactivity of SO_3^{2-}, as compared to water, has also been reported in the substitution reaction of the dimethylglyoxime intermediate[8a] $Co(DH)_2SO_3^-$, for which $k_s/k_w = 650$. The formal positive charge of $Co(en)_2SO_3^+$ would be consistent with a higher reactivity toward SO_3^{2-} than toward $Co(DH)_2SO_3^-$. Likewise the reactivity ratio k_s/k_w falls[3b] to a lower value of about 80 with the triply negative species $Co(CN)_4SO_3^{3-}$. Since our studies of $Co(en)_2SO_3OH$ show that $k_{OH^-}/k_{SO_3^{2-}} \geq 50$, then it follows that OH^- is at least 4×10^5 times more reactive than OH_2 as a nucleophile toward $Co(en)_2SO_3^+$. This order of reactivity correlates with the basicity of the nucleophiles OH^-, SO_3^{2-}, and OH_2. A value of $k_{OH}/k_w = 10^3$ has been reported[9] for the negatively charged species $Co(CN)_5^{2-}$.

The limiting SN1 mechanism (eq VI and V) requires that, at high nucleophile concentration, a limiting rate equivalent to k_{-w} should be attained. This was observed, within experimental error, for the nucleophiles SO_3^{2-}, HSO_3^-, and N_3^-. The rapid exchange of the aquo ligand in *trans*-$Co(en)_2SO_3OH_2^+$ with solvent $H_2{}^{18}O$ is in accord with this mechanism.

At pH 8.1, the functional dependence of k_{obsd} upon $[SO_3^{2-}]$ is also consistent with an SNIP mechanism but this would require an ion-pair stability constant of $(1.5 \pm 0.5) \times 10^2$ for $Co(en)_2SO_3OH_2^+, SO_3^{2-}$. This seems improbably large for the ionic strength (1 *M*) employed in these experiments. Likewise for azide substitution, a stability constant exceeding 10^2 for the 1:1 ion pair $Co(en)_2SO_3OH_2^+,N_3^-$ would be required for this SNIP mechanism and this argues against the alternative ion-pair mechanism. Moreover, a limiting SN1 mechanism has been demonstrated for substitution of $Co(en)_2SO_3OH$ and this would probably persist with the corresponding aquo complex.

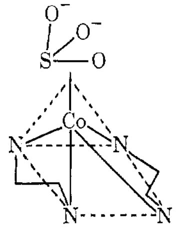
***trans* Activation by Sulfito Ligands.**—The enhanced lability due to the sulfito ligand in *trans*-$Co(en)_2(SO_3)_2^-$, *trans*-$Co(en)_2SO_3OH$, and *trans*-$Co(en)_2SO_3OH_2^+$ is derived almost wholly from the relatively low $\Delta H^\ddagger$ values for dissociative releases of the ligands *trans* to sulfito. Table IV summarizes the activation parameters deduced in the present study. As a single comparison system, the *trans* → *cis* isomerization of $Co(en)_2OHOH_2^{2+}$ is cited[10] in Table IV since this is quoted as a "labile" species[11] which may isomerize[12] by dissociative release of an aquo ligand. At 25°, release of an aquo ligand from *trans*-$Co(en)_2SO_3OH_2^+$ is 3700 times faster than from *trans*-$Co(en)_2OHOH_2^{2+}$ and this rate difference is almost wholly accommodated by the lower $\Delta H^\ddagger$ value for the sulfito complex. Since most other diamagnetic cobalt(III) complexes[11] substitute with $\Delta H^\ddagger$ values ranging from 25 to 30 kcal mol^{-1}, these low $\Delta H^\ddagger$ values for sulfito complexes appear to be a singular property arising from the sulfito ligand. Even dissociative release of azide from $Co(CN)_5N_3^-$ exhibits[9] $\Delta H^\ddagger = 27.3$ kcal mol^{-1} and dissociative aquo release from $Co(CN)_5OH_2^{2-}$ exhibits $\Delta H^\ddagger = 30$ kcal mol^{-1}.

The origin of the low $\Delta H^\ddagger$ values and, hence, the labilization effect by sulfito ligands must lie in differences in bond energy terms between the ground state and the transition state leading to the dissociated intermediate $Co(en)_2SO_3^+$. Structural information on related sulfito complexes does not provide strong evidence for weakening of the metal–ligand bond *trans* to the sulfito ligand in the ground state. In *trans*-$Co(en)_2NCS \cdot SO_3$, the Co–N bond length[13] is 1.969 ± 0.015 Å for Co–NH₂ as compared to 1.974 ± 0.015 Å for the Co–NCS bond *trans* to the sulfito ligand. In contrast, there is some evidence in Pt(II) complexes that *trans* activating ligands cause significant lengthening of metal–ligand bonds.[11]

Stronger Co–S π bonding in the dissociated intermediate, as compared to the ground state, could lead to reduced $\Delta H^\ddagger$ values. Mössbauer studies[14] of iron complexes suggest that the order of π-bonding ability is $CN^- > SO_3^{2-} > NO_2^- \sim NH_3$. It should be noted that the cyano ligand is much less effective than the sulfito ligand in reducing $\Delta H^\ddagger$ for dissociative reactions in cobalt(III) complexes. Moreover metal-to-ligand π bonding in dimethylglyoxime complexes like $Co(DH)_2(NO_2)OH_2$ and $Co(DH)_2(I)OH_2$ is not associated with high reactivity.[3a] These lines of evidence argue against π bonding as the cause of low $\Delta H^\ddagger$ values for sulfito complexes. The ineffectiveness of the iodo ligand, which has a low electronegativity and is highly polarizable, suggests also that these properties are not crucial factors in the effectiveness of sulfur as the sulfito ligand.

The *trans*-sulfito complexes of cobalt(III) show some resemblance to vitamin B_1 complexes[15] in that both exhibit strong *trans* labilization and substantial stability for five-coordinate intermediates. The vitamin B_1 complexes exhibit some characteristics of the cobalt(II) state even though their formal oxidation state is cobalt(III). The reducing nature of the sulfito ligand might suggest an excited state involving partial charge transfer as an intermediate but the stereospecificity observed here for the sulfito substitutions is difficult to reconcile with this mechanism.

One unusual characteristic of the sulfito ligand is its potential ability to bond either through sulfur or through oxygen.[16] (An analogous example arises[17] in $Pd(DMSO)_4^{2+}$ where two DMSO ligands are bonded through sulfur and two through oxygen.) In the ground state of the *trans*-sulfitocobalt(III) complexes, the bonding is through sulfur. Dissociation to yield a pseudotetragonal intermediate $Co(en)_2SO_3^+$ provides the possibility of forming a three-center π–π bond utilizing the empty E_g Co(III) orbital



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This would achieve considerable stabilization of this intermediate and relatively low $\Delta H^{\ddagger}$ values. Stereospecificity would be achieved by entry of the incoming nucleophile below the tetragonal plane as the ethylenediamine ligands revert to their ground-state octahedral sites.

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Normal Equations for the Gaussian Least-Squares Refinement of Formation Constants with Simultaneous Adjustment of the Spectra of the Absorbing Species

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This paper describes the salient features in the derivation of the normal equations appropriate to the calculation of molar absorptivities and formation constants from spectrophotometric data. Since concentration errors are common to all the measurements on a solution, a nondiagonal weight matrix is required if spectrophotometric measurements are made at more than one wavelength. This matrix is approximately diagonal for spectrophotometric errors of a few thousandths of 1 absorbance unit and concentration errors of a few tenths of 1%. Even when concentration errors are more significant, accurate estimates of the parameters and of χ^2, but not necessarily of the correlation coefficients, are obtained when the off-diagonal elements are neglected. Calculations on data for iron(III)–chloride complexes in DMSO are described; the constants for the stepwise formation of $FeCl^{2+}$ and $FeCl_2^+$ are $(5.5 \pm 2.6) \times 10^4$ and $280 \pm 17\ M^{-1}$ and the molar absorptivities of these species are 1045 ± 9 and 1960 ± 20, respectively, at 400 nm.

Introduction

Spectrophotometric measurements have long been used to determine formation constants.[1] For those situations in which the spectra of the absorbing species are not known, various graphical techniques have been developed to evaluate the formation constants and molar absorptivities simultaneously.[2,3] Numerical search techniques have been used to estimate the least-squares parameters from spectrophotometric[4] and mathematically equivalent calorimetric data.[5] Newton and Baker,[6] Hugus,[7] and Prasad and Peterson[8] have applied Gaussian least-squares procedures to spectrophotometric[6,8,9] and calorimetric data.[10] However these treatments do not take cognizance of the strong correlation among the analytical errors if measurements are made at more than one wavelength.

The present paper describes the salient features of the derivation of the normal equations appropriate to the multiwavelength problem. The correlation of the analytical errors makes this an unusual and interesting application of the Gaussian method of least squares. Data for the iron (III)–chloride system in DMSO[9] are reevaluated. Complex formation between $Cu(tfac)_2$ and pyridine in benzene solvent[11] and between Hg(II) and iodide in DMSO solvent[12] is the subject of other communications.

The General Normal Equations

The *modus operandi* of a least-squares analysis is to estimate the error-free values associated with a series of measurements by minimizing the sum of the squares of the differences between the experimental values and "adjusted" values where each term is weighted as the reciprocal of its variance.[13] Note that one does not proceed to minimize the sum of the squares of some condition function with a weighting function calculated from propagation of error formulas. When these two approaches are equivalent, the second may be derived from the first.

In the spectrophotometric problem discussed here, we have the possibility of errors in the total metal concentration, in the total ligand concentration, and in the spectrophotometric measurement itself. Consequently, $\mathcal{S}$, the weighted sum of the squares of the

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