isocyanide ($CNCOC(CH_3)_3$)[9] instead of benzoyl isocyanide, the monoadduct **2b** is also formed (IR (Nujol) $\nu(C{\equiv}N)$ 1970 cm^{-1}, $\nu(C{=}O)$ 1720 cm^{-1}) together with the bis adduct **3b** (IR (Nujol) $\nu(C{\equiv}N)$ 2045 cm^{-1}, $\nu(C{=}O)$ 1745 cm^{-1}).[10] This behavior parallels nicely that of CO complexation to $Fe^{II}TPP$.[6]

Reaction between **3a** and 1 equiv of pyridine in CH_2Cl_2 (20 °C) gives **4a**, which has been crystallized by CH_3OH addition as a red-purple solid whose elemental analysis and mass spectrum[11] agree with the formula $C_{57}H_{38}N_6OFe$ (electronic spectrum (toluene) λ_{max} 424 nm (ϵ 4.3 × 10^5), 534 nm (ϵ 1 × 10^4)). The ^{13}C NMR spectrum of **4a** (CD_2Cl_2, 20 °C, $SiMe_4$) exhibits a sharp peak at 186 ppm, which can only be observed when the compound is prepared from $^{13}CNCOC_6H_5$ (porphyrin ring 145, 142.6, 134.7, 134.1, 127.1, 126.9, 121.7 ppm; pyridine 146.1, 133.8, 120 ppm; $CN^{13}COC_6H_5$ 150.07 ppm; free $C^{13}NCOPh$ 165 ppm[9]). In deoxygenated solvents like C_6H_6 or $C_6H_5CH_3$, complex **4a** is stable indefinitely and is slowly transformed into the known $FeTPP(py)_2$ only by further addition of a large excess of pyridine. However, in aerated solution, the $FeTPP(CNCOC_6H_5)(py)$ is irreversibly oxidized to the μ-oxo dimer $(FeTPP)_2O$ (10^{-4} M, benzene, 8% after 24 h). In comparison FeTPP(py)(CO) is more sensitive to dioxygen under identical conditions ($t_{1/2}$ = 0.5 h).[12] The preparation of other mixed hexacoordinated complexes can be realized similarly with 1-methylimidazole (electronic spectrum (toluene) λ_{max} 428 nm (ϵ 4 × 10^5), 539 nm (ϵ 1.05 × 10^4); IR (Nujol) $\nu(C{\equiv}N)$ 1980 cm^{-1}, $\nu(C{=}O)$ 1690 cm^{-1}) and 4-cyanopyridine (electronic spectrum (toluene) λ_{max} 424 nm (ϵ 4.1 × 10^5), 532 nm (ϵ 1.1 × 10^4); IR (Nujol) $\nu(C{\equiv}N)$ 2020 cm^{-1}, $\nu(C{=}O)$ 1700 cm^{-1}), thus providing models for isocyanide binding to myoglobin.[13]

Determination of the isocyanide stretching frequencies in heme isocyanides provides an opportunity to demonstrate clearly the sensitivity of ligand binding to the electronic properties of the second axial ligand and the porphyrin. For example, the data in Table I demonstrate that the *N*-acyl isocyanide group is more sensitive than alkyl isocyanide ligands to changes in the electronic environment. Reduction of the $C{\equiv}N$ stretching frequency relative to the free ligand value is $\Delta\nu$ = 60 cm^{-1} for **3a**, while the $CN{-}C(CH_3)_3$ frequency does not show a significant shift upon complexation to form $[Fe^{II}TPP(CNC(CH_3)_3)_2]$.[7] The $\nu(C{\equiv}N)$ shift indicates that the bond order of the C–N bond decreases in $CNCOC_6H_5$. This is consistent with a greater π-acceptor ability of the *N*-acyl isocyanide group compared with that of the $CNC(CH_3)_3$ ligand and with a concomitant increase in back-π-bonding from iron to the $C{\equiv}N$ bond.

Mössbauer results reported in Table II provide further evidence for the analogy between CO and CNCOR. Trends in both isomer shift δ and quadrupole splitting ΔE_Q in $FeTPP(CNCOC_6H_5)_2$ and $FeTPP(CNCOC_6H_5)(py)$ parallel those found in the corresponding CO adducts:[15,16] *N*-acyl isocyanide like carbon monoxide significantly reduces the observed splitting relative to the ferroporphyrin bis(amine).[16]

We are currently studying the chemical properties of *N*-acyl isocyanides bound to hemoproteins.

Experimental Section

5,10,15,20-Tetraphenylporphyrin, $TPPH_2$, was prepared by the standard procedure from benzaldehyde and pyrrole in refluxing propionic acid.[17] The iron complex FeTPP(Cl) was prepared from $FeCl_2{\cdot}4H_2O$ and tetraphenylporphyrin in DMF.[18]

$FeTPP(CNCOC_6H_5)_2$ (3a). In a typical experiment, a solution of **1** (0.2 g, 0.29 mmol) in CH_2Cl_2 (20 mL) was treated under argon with 2 equiv of $CNCOC_6H_5$ (0.08 g, 0.6 mmol) in 2 mL of CH_2Cl_2 (–40 °C). The reaction was stirred for 10 min. After addition of 70 mL of CH_3OH, purple crystals of **3a** formed, which after 24 h at –40 °C were collected by filtration and vacuum-dried (0.23 g, 85%). Anal. Calcd for $C_{60}H_{38}N_6O_2Fe$: C, 77.41; H, 4.09; N, 9.03. Found: C, 77.82; H, 4.35; N, 8.71.

$FeTPP(CNCOC(CH_3)_3)_2$ (3b). The reaction of **1** with a large excess of $CNCOC(CH_3)_3$ yields pure **3b** in 78% yield. ^1H NMR (–40 °C, $CDCl_3$, $SiMe_4$): 8.76 (s, 8 H), 8.15 (m, 8 H), 7.8 (m, 12 H), –0.45 (s, 18 H) ppm. Mass spectrum: *m/e* 668 $(FeTPP)^+$, 111 $(CNCOC(CH_3)_3)^+$. Electronic spectrum (toluene): λ_{max} 430 nm (ϵ 4.05 × 10^5), 552 nm (ϵ 1.1 × 10^4), 593 nm (ϵ 6.5 × 10^3).

$FeTPP(CNCOC_6H_5)(py)$ (4a). A 150-mL Schlenk flask was charged with 0.2 g (0.21 mmol) of **3**, 20 mL of CH_2Cl_2, and a stir bar under argon (20 °C). Then 1 equiv of pyridine (0.016 g) in 5 mL of CH_2Cl_2 was added and the reaction mixture stirred for 5 min, after which 80 mL of CH_3OH was added and the resulting solution filtered, giving red-purple crystals in 92% yield (0.17 g). Anal. Calcd for $C_{57}H_{38}N_6OFe$: C, 77.97; H, 4.33; N, 9.57. Found: C, 77.31; H, 4.21; N, 9.10.

Instrumentation. Infrared spectra were recorded on a Unicam SP 1100 spectrophotometer. Mössbauer spectra were recorded with a $^{57}Co(Rh)$ source. Mass spectra were recorded by using a Varian MAT 311 spectrometer. ^1H NMR spectra were obtained at 80 MHz and proton-decoupled ^{13}C NMR spectra were obtained at 20 MHz in the pulse-Fourier-transform mode with a Bruker WT 80 DS spectrometer. Ultraviolet spectra were recorded with a Jobin Yvon Hitachi spectrophotometer.

Acknowledgment. We thank Professor F. Varret for his contribution to the Mössbauer work.

Registry No. **1**, 16591-56-3; **2b**, 92958-46-8; **3a**, 92958-47-9; **3b**, 92958-48-0; **4a**, 92958-49-1; $FeTPP(CNCOC(CH_3)_3)(B)$ (B = 1-methylimidazole), 92958-50-4; $FeTPP(CNCOC(CH_3)_3)(B)$ (B = 4-cyanopyridine), 92958-51-5.

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Kinetics and Mechanism of the Reactions of Sulfito Complexes in Aqueous Solution. 6. Formation, Aquation, and Intramolecular Electron Transfer of the *cis*-Aquo(sulfito-*O*)bis(ethylenediamine)cobalt(III) Ion[1]

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In previous studies it has been shown that aquopentaammine,[2] aquo(tetraethylenepentamine)[3] ("tetren"),

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and diaquo(2,2′,2″-triaminotriethylamine) ("tren") cobalt(III),[4] as well as aquopentaammineplatinum(IV)[1] complex ions rapidly equilibrate (stopped-flow time scale) in mildly acidic aqueous sulfite solution according to the general scheme

$$ML_5OH + SO_2 \rightleftarrows ML_5OSO_2^- + H^+$$

Subsequent processes include sulfite O- to S-bonded isomerization, internal redox, or further sulfite addition, depending on the identity of M and of the L_5 moiety. The tren species was chosen to determine the effect of changing to a diaquo complex while avoiding possible complications due to cis to trans isomerization, which readily occurs with the closely related bis(ethylenediamine) ($(en)_2$) congeners.[5] We now report rate studies and the mechanistic interpretation of SO_2 uptake by *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ ion, the acid hydrolysis of the O-bonded sulfito product, and some preliminary data on the internal electron-transfer reaction.

Experimental Section

Materials. (Carbonato)bis(ethylenediamine)cobalt(III) chloride was prepared in the solid form by a published procedure.[6] The purity of the compound was checked by microanalysis.[7] Anal. Calcd for $[Co(en)_2CO_3]Cl$: C, 21.87; H, 5.83; N, 20.42. Found: C, 21.88; H, 5.81; N, 20.38.

Diaquobis(ethylenediamine)cobalt(III) ions were prepared in situ by acidification of $[Co(en)_2CO_3]Cl$ solution. Portions of the carbonato complex were dissolved in ice-cold 1.0 M $HClO_4$, diluted with CO_2-free water, placed in an ice bath, and bubbled with N_2 for a period of 2 h to free the solution of dissolved CO_2. The pH of the solution was then adjusted to 3 by careful addition of a concentrated solution of NaOH and stored at 5 °C to minimize the rate of isomerization of cis to trans forms.[5] The spectrum of the solution determined in a Cary 118 spectrophotometer is in reasonable agreement with that found in the literature.[8] All chemicals used were of reagent grade, and deionized/degassed water was used in preparing all solutions. Solid $Na_2S_2O_5$ was used as the source of sulfite as discussed earlier.[2]

Rate Measurements. The "pH-jump technique" using the automated Durrum Model 110 stopped-flow spectrometer assembly previously designed to study CO_2-uptake reactions[9] was employed in a similar manner to study the SO_2-uptake process. In this procedure one reservoir syringe of the stopped-flow device is filled with the McIlvaine[10] phosphate–citric acid buffer in which an appropriate amount of $Na_2S_2O_5$ is dissolved and the second syringe with a solution of diaquo complex. The ionic strength of both solutions is adjusted to 1 M by adding calculated quantities of sodium perchlorate. At the pHs of the experiments the rate of SO_2 uptake is very much faster than cis to trans isomerization[5] of the diaquo reactant, so no interference occurs. It is safe to assume that the *O*-sulfito product is in the cis form, since immediate addition of excess acid eliminates SO_2 from the complex, yielding the original *cis*-diaquo starting material.

The SO_2-elimination process was studied more or less as described previously.[2–4] The O-bonded (sulfito)bis(ethylenediamine)cobalt(III) complex is produced in situ by dissolving the appropriate volume of stock diaquo complex solution and $Na_2S_2O_5$ in the molar ratio of 1:2 with the solution adjusted to approximately pH 5.5. A fresh solution of sulfito complex is made before each run. It is then stored at 0 °C until the actual run is made, utilizing the pH-jump procedure already described. The SO_2-uptake and -elimination processes were studied at 400 nm where the difference in absorbance between reactant and product is at a maximum. The solutions were collected after each stopped-flow run, and pH measurements were performed immediately. The observed pseudo-first-order rate constants were collected in the usual way using a least-squares program and are reported as an average of at least six runs.

The slow redox reaction of the O-bonded sulfito complex was followed on a Cary Model 118C spectrophotometer utilizing time-drive chart procedure. For these reactions, solutions prepared in a similar way as in the SO_2-uptake experiments were thermostated at the reaction temperature, mixed in a volumetric flask, and rapidly transferred to a thermostated 1-cm cuvette. The pH of each solution was measured after mixing using a water-jacketed sample holder thermostated at the reaction temperature. The redox reactions were studied at 400 nm, and the observed first-order rate constants were calculated by a conventional least-squares procedure from the absorbance vs. time data.

Results and Discussion

An almost instantaneous color change from pink to orange occurs when $Na_2S_2O_5$, $NaHSO_3$, or Na_2SO_3 is added to buffered solutions of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ at a pH between 4 and 7, indicating the formation of O-bonded sulfito complex.[11] The solution containing sulfito complex slowly converts to the almost colorless solution characteristic of Cobalt(II). The concentration of O-bonded sulfito complex can be optimized at pH 5.5 in fourfold excess sulfite concentration. Attempts to isolate the O-bonded intermediate were unsuccessful due to the subsequent redox decomposition of the species in the accessible pH range.

The SO_2-uptake kinetics study was performed in the range of $10.1 < t < 25$ °C and $5.2 < pH < 6.8$. The data obtained are summarized in Table I. The magnitudes of the overall absorbance increase and the final absorbance depend on the SO_2 concentration as well as the pH of the solution. These magnitudes, however, remain constant at pH >5.5 and decrease with decreasing pH until the extent of reaction becomes negligible. Such observations are consistent with the concept of an equilibrium system in which the reverse process makes an increasingly significant contribution as the acidity increases. The data in Table I have been treated on the basis of the mechanism stated in Scheme I. This scheme is analogous to that used in previous CO_2- and SO_2-uptake studies. It does differ somewhat from that proposed for the tren analogue[4] in that we find here no conclusive evidence for direct reaction of the diaquo complex[12] with SO_2. It is, however, consistent with the fact that neither fully protonated aquopentaammine- nor aquo(tetren)cobalt(III) complexes appear to take up directly either SO_2[2,3] or CO_2.[13]

The rate law for the formation and decomposition of O-bonded sulfito complexes corresponding to Scheme I takes the form

$$\frac{d \ln [\text{aquo complex}]_T}{dt} = k_{obsd} = k_1\alpha_1[SO_2] + k_2\alpha_2[SO_2] + k_{-1}\beta_1 + k_{-2}\beta_2 \quad (1)$$

In this α_1 and α_2 are the fractions of aquo hydroxo and dihydroxo species, respectively, at a given pH and temperature.

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(11) The characteristic peak for the O-bonded sulfito complexes is near 300 nm with a lower extinction coefficient than for S-bonded species. In the present case the peak is at 310 nm with an extinction coefficient of 1500, which is comparable to $\lambda_{max} = 330$ nm ($\epsilon \sim 2100$)[2] for $[Co(NH_3)_5(OSO_2)]^+$, $\lambda_{max} = 330$ nm ($\epsilon = 1928$)[3] for ($\alpha\beta S$)–$[Co(tetren)(OH_2)(OSO_2)]^+$, and $\lambda_{max} = 325$ nm ($\epsilon = 1825$)[4] for $[Co(tren)(OH_2)(OSO_2)]^+$.

(12) In the study of the tren complex,[4] it was found that the data were best fitted by including in the reaction scheme $[Co(tren)(OH_2)_2]^{3+} + SO_2 \rightarrow [Co(tren)(OH_2)(OSO_2H)]^{2+} + H^+$. The rate constant for this reaction was found to be less than 10% that of the corresponding reaction with $[Co(tren)(OH)(OH_2)]^{2+}$ ion, and its reality is somewhat open to question due to the errors inherent in the analysis of data.[4]

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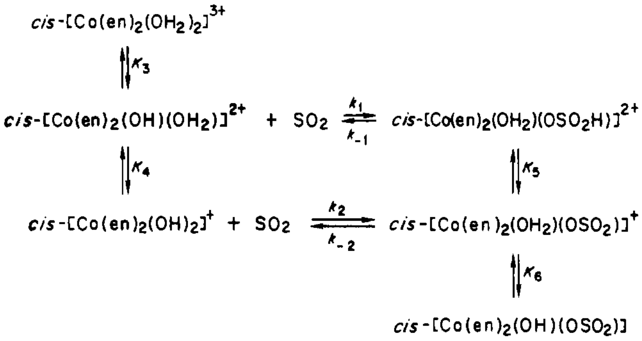
Table I. Dependence of Observed Rate Constant on pH for SO_2 Uptake by *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ [a]

pH	k_{obsd}, s^{-1}	temp, °C	pH	k_{obsd}, s^{-1}	temp, °C
5.24	41.7 ± 0.6	10.1	5.50	54.5 ± 0.9	15.0
5.38	42.7 ± 0.8	10.1	5.54	50.1 ± 1.0	15.0
5.48	35.2 ± 0.4	10.1	5.65	47.1 ± 1.0	15.0
5.50	42.0 ± 0.5	10.1	5.72	46.0 ± 0.9	15.0
5.54	38.7 ± 0.3	10.1	5.80	42.5 ± 0.8	15.0
5.55	44.5 ± 0.5	10.1	5.85	39.3 ± 0.7	15.0
5.59	37.6 ± 0.6	10.1	5.95	25.6 ± 0.8	15.0
5.65	41.0 ± 0.8	10.1	5.26	84.3 ± 1.5	19.1
5.70	34.6 ± 0.6	10.1	5.36	84.0 ± 2.0	19.1
5.73	33.9 ± 0.3	10.1	5.49	72.5 ± 2.2	19.1
5.75	44.5 ± 0.8	10.1	5.59	71.5 ± 1.6	19.1
5.90	23.0 ± 0.3	10.1	5.65	65.0 ± 2.0	19.1
6.03	19.1 ± 0.6	10.1	5.86	52.0 ± 1.0	19.1
6.15	17.1 ± 0.2	10.1	6.15	35.0 ± 0.9	19.1
6.20	11.3 ± 0.2	10.1	5.50	101 ± 3.0	25.0
6.20	14.3 ± 0.3	10.1	5.59	90.0 ± 2.5	25.0
6.25	9.12 ± 0.1	10.1	5.70	80.0 ± 2.0	25.0
6.35	6.26 ± 0.1	10.1	5.80	65.0 ± 1.8	25.0
6.40	5.03 ± 0.2	10.1	5.95	62.0 ± 1.5	25.0
6.88	1.90 ± 0.1	10.1	6.10	45.0 ± 1.0	25.0

[a] Conditions: [complex] = 2 × 10^{-3} M; $[S]_T$ = 0.02 M; I = 1.0 M ($NaClO_4$).

Scheme I. Mechanism for Sulfur Dioxide Uptake by the *cis*-Diaquobis(ethylenediamine)cobalt(III) Ion



These fractions may be calculated from the relations

$$\alpha_1 = K_3[H^+]/([H^+]^2 + K_3[H^+] + K_3K_4) \quad (2)$$

$$\alpha_2 = K_3K_4/([H^+]^2 + K_3[H^+] + K_3K_4) \quad (3)$$

and the known values[14] of K_3 and K_4 and the observed pHs. Similarly, β_1 and β_2 are the fractions of aquo bisulfito and aquo sulfito species, respectively, at a given pH and temperature. If K_5 and K_6 are known, these fractions may be computed from the relations

$$\beta_1 = [H^+]^2/([H^+]^2 + K_5[H^+] + K_5K_6) \quad (4)$$

$$\beta_2 = K_5[H^+]/([H^+]^2 + K_5[H^+] + K_5K_6) \quad (5)$$

Also, the SO_2 concentration may be calculated at each pH from the equation[15] (S_T = total free sulfite in solution)

$$[SO_2] = [H^+]^2[S_T]/([H^+]^2 + K_1[H^+] + K_1K_2) \quad (6)$$

At low $[H^+]$, where contribution by the reverse SO_2-elimination process is negligible (pH >5.0), eq 1 reduces to

Table II. Temperature Dependence of Derived Rate Constants for SO_2 Uptake by *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ [a]

temp, °C	$10^{-7}k_1$, M^{-1} s^{-1}	$10^{-10}k_2$, M^{-1} s^{-1}
10.1	5.87 ± 0.29	0.10 ± 0.10
15.0	7.17 ± 0.54	3.80 ± 0.18
19.1	8.46 ± 0.21	0.22 ± 0.10
25.0	10.5 ± 0.50	2.16 ± 0.17

$\Delta H_1^{\ddagger} = 6.02 + 0.05$ kcal mol^{-1}
$\Delta S_1^{\ddagger} = -1.6 + 0.2$ cal mol^{-1} deg^{-1}

[a] Conditions: [complex] = 2 × 10^{-3} M; I = 1 M ($NaClO_4$).

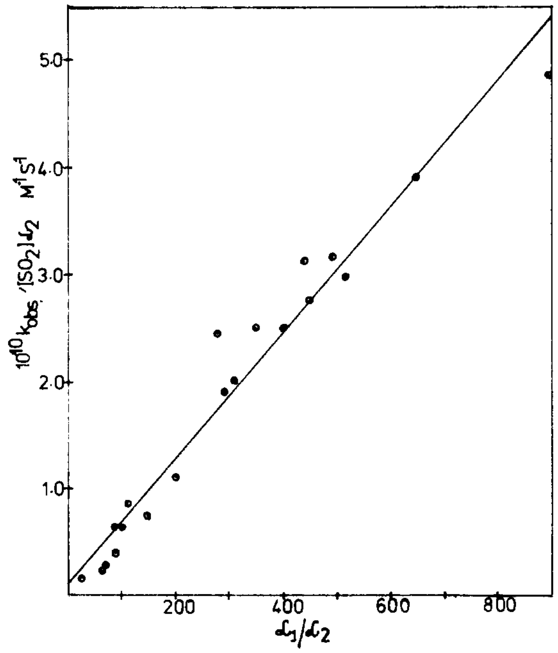


Figure 1. Plot of $k_{obsd}/\alpha_2[SO_2]$ vs. α_1/α_2 for the SO_2 uptake by *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ at 10.1 °C.

$$k_{obsd} = (k_1\alpha_1 + k_2\alpha_2)[SO_2] \quad (7)$$

That is

$$k_{obsd}/\alpha_2[SO_2] = k_1\alpha_1/\alpha_2 + k_2 \quad (8)$$

The values of k_1 and k_2 were obtained by a linear regression analysis of the experimental data using eq 8 and are summarized in Table II. A graphical representation of such an analysis of the data at 10.1 °C is presented in Figure 1. It is evident from Table II that k_2 is subject to large errors in spite of the small standard deviations for the sets of data at each temperature. One can only conclude that this rate constant is approaching the diffusion-controlled limit, as was found to be the case for SO_2 uptake by the tren congener.[4]

The value of k_1 may also be determined by rearranging eq 7 to the form

$$k_{obsd}/\alpha_1[SO_2] = k_1 + k_2\alpha_2/\alpha_1 \quad (9)$$

The contribution from the k_2 term can be neglected since $\alpha_2/\alpha_1 = K_4/[H^+]$ and $K_4 \ll [H^+]$ in the experimental pH range. The average value of $k_{obsd}/\alpha_1[SO_2]$ for runs at 10.1 °C yields the figure $k_1 = (6.1 \pm 1.5) \times 10^7$ M^{-1} s^{-1}, which is in good agreement with the Table II data, confirming the internal consistency of the procedure. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for k_1, calculated by means of a computerized least-squares program, are also presented in Table II.

The variation of the SO_2-uptake rate with total sulfite concentration was studied at a constant pH of 4.8 and at 10.1 °C. The data obtained are listed in Table III. These data when plotted as k_{obsd} vs. $[SO_2]$ give a good straight line with a small intercept (Figure 2). Linear regression analysis of the data yields a slope of $(3.6 \pm 0.1) \times 10^6$ M^{-1} s^{-1} and an

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(14) The values of K_3 and K_4 are reported[8] to be 8.71 × 10^{-7} and 6.46 × 10^{-9} M^{-1} at 25 °C and I = 1.0 M ($NaNO_3$). These values were used in our experiments without adjustment for the changed electrolyte or temperature variations, since such adjustments are known to be small. For example, it has been demonstrated[4] that the corresponding constants for the tren congener undergo only modest changes within the range 6–25 °C, or on reducing the ionic strength to 0.5 M. In any case such variations will not affect the conclusions drawn from our data.

(15) The values of K_1 are interpolated from the previously published data.[4] They are 1.82 × 10^{-2}, 1.58 × 10^{-2}, 1.41 × 10^{-2}, and 1.26 × 10^{-2} M^{-1} at 10, 15.1, 19, and 25 °C, respectively. K_2 is temperature independent within the present range[4] where it has a value of 5.01 × 10^{-7} M^{-1}.

Table III. Dependence of Observed Rate Constant on SO_2 Concentration for SO_2 Uptake by *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ [a]

$[S]_T$, M	$10^5 \times [SO_2]$, M	k_{obsd}, s^{-1}	$[S]_T$, M	$10^5 \times [SO_2]$, M	k_{obsd}, s^{-1}
0.01	0.84	44 ± 2	0.04	3.38	140 ± 4
0.02	1.69	77 ± 2	0.06	5.04	201 ± 4
0.03	2.52	108 ± 3	0.10	8.43	320 ± 5

[a] Conditions: [complex] = 2×10^{-3} M; temp, 10.1 °C; $I = 1$ M ($NaClO_4$); pH 4.80.

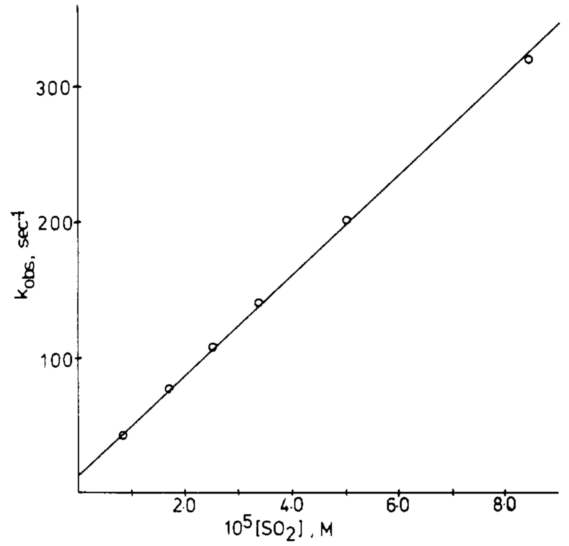

Figure 2. Plot of k_{obsd} for SO_2-uptake reaction vs. $[SO_2]$ at pH 4.8 and 10.1 °C.

intercept of (16 ± 2) s^{-1}. The results can be rationalized by considering eq 1 in the reduced form

$$k_{obsd} = k_1\alpha_1[SO_2] + k_{-1}\beta_1 \qquad (10)$$

since at pH 4.8 the contributions by k_2 and k_{-2} can be assumed to be quite small. The k_1 value calculated from the slope of the plot according to eq 10 is 6.9×10^7 M^{-1} s^{-1}, which is fairly close to the corresponding values obtained from the data presented in Table II (5.9×10^{-7} M^{-1} s^{-1}) and as computed from eq 9 (6.1×10^7 M^{-1} s^{-1}). The slightly higher values obtained in this case and from eq 9 for k_1 may be due to the contribution by the fraction of dihydroxo species, which is neglected in eq 9 and 10. The intercept ($k_{-1}\beta_1$) is the contribution of the reverse process, i.e. elimination of SO_2.

In order to know more about the magnitude of this latter contribution, some SO_2-elimination reactions were studied at 10.1 °C in the range 3.28 < pH < 4.68. In this pH range, α_2 and β_2 can safely be assumed to be small. Equation 10 can thus be applied again, with β_1 becoming $[H^+]/([H^+] + K_5)$ in this lower pH range, since K_5K_6 is sure to be much smaller than $[H^+]^2$ or $K_5H^+]$. From the known value at 10.1 °C of k_1 (5.87×10^7 M^{-1} s^{-1}; Table II), $k_{-1}\beta_1$ values were calculated and are presented in Table IV. It is seen that $k_{-1}\beta_1$ varies linearly with $[H^+]$ (last column of Table IV), indicating that $K_5 \ll [H^+]$, so that $k_{-1}\beta_1/[H^+] = k_{-1}/K_5$. Using the average value of $k_{-1}\beta_1/[H^+] = 7.52 \times 10^5$ and the known $[H^+]$ at pH 4.8, one evaluates $k_{-1}\beta_1 = 12 \pm 1$ s^{-1} at this acidity, in reasonable agreement with the 16 ± 2 s^{-1} value previously derived from Figure 2. The magnitude of β_1 can only be estimated, but a good approximation based on the tren study[4] is 3×10^{-4} at 10 °C. This suggests that k_{-1} at this temperature must be about 2×10^{-2} s^{-1}. This is to be compared with the value of approximately 1×10^{-2} s^{-1} for the tren analogue[4] and 5×10^{-2} s^{-1} for the tetren species.[3]

A preliminary investigation was carried out on the redox decomposition of *cis*-$[Co(en)_2(OH_2)(OSO_2)]^+$. As mentioned previously (see Experimental Section), the spectral analysis of the light pink solution obtained at pHs lower than 7.0 suggested nearly complete conversion of the cobalt(III) complex to cobalt(II). Cobalt(II) was identified in the solution by the tetrakis(thiocyanato)cobaltate(II) method.[16] The kinetics of the redox decomposition was studied over the pH range 3.00 < pH < 6.60. In this pH range there is no spectral evidence for chelation or substitution for the second aquo ligand by SO_3^{2-} to yield a bis(sulfito) end product.[17] The values of the observed pseudo-first-order rate constants, k_{obsd}, obtained at the total sulfite concentration of 0.01 M, at 25 °C, and at the various acidities employed are presented in Table V. It is obvious from Table V that k_{obsd} increases slightly as the pH increases but appears to level out at a constant value of 5×10^{-4} s^{-1} at pH ~5. This, again, parallels closely the behavior of the tren congener,[4] where the limiting value of k_{obsd} at 25 °C is 10^{-3} s^{-1}. Above pH 5, however, k_{obsd} for the $(en)_2$ species again appears to increase, but now it is entirely possible that cis → trans isomerization[17] is complicating the process. In the lower pH range 3 < pH < 5, the data may be analyzed according to the mechanism suggested[4] for the redox decomposition of $[Co(tren)(OH_2)(OSO_2)]^+$ ion. However, a more detailed investigation of the present system is required before a complete discussion of this complicated reaction can be given. Further work on this project is now in progress in our Jamaica laboratory.

Table IV. pH Dependence of the Rate Constants for the Elimination of SO_2 from *cis*-$[Co(en)_2(OH_2)(OSO_2H)]^{2+}$ at 10.1 °C[a]

pH	k_{obsd}, s^{-1}	$k_{-1}\beta_1$,[a] s^{-1}	$10^{-5}k_{-1}\beta_1/[H^+]$, M^{-1} s^{-1}
3.28	435 ± 12	413	7.87
3.32	403 ± 11	381	7.47
3.52	247 ± 10	225	7.61
3.60	213 ± 10	191	7.41
3.75	154 ± 5	132	7.41
3.95	106 ± 3	84	7.49
4.31	58.5 ± 2	36.7	7.49
4.40	51.8 ± 1.0	30.2	7.59
4.48	45.8 ± 1.0	24.3	7.34
4.60	39.2 ± 1.1	18.0	7.16
4.68	36.5 ± 1.0	15.5	7.40
			7.52 ± 0.23 (mean)

[a] [complex] = 2 mM; $[S]_T$ = 8 mM; I = 1.0 M (citrate/phosphate). [b] Calculated from eq 9 with $k_1 = 5.87 \times 10^7$ M^{-1} s^{-1}.

Table V. Rate Data for the Redox Decomposition of *cis*-$[Co(en)_2(OH_2)OSO_2]^+$ [a]

pH	10^4k_{obsd}, s^{-1}	pH	10^4k_{obsd}, s^{-1}	pH	10^4k_{obsd}, s^{-1}
3.00	4.31	3.82	5.20	5.20	6.20
3.21	4.34	4.05	5.32	5.70	6.50
3.25	4.51	4.48	5.92	5.78	6.69
3.50	4.62	4.82	5.96	6.10	7.02
3.68	4.80	4.94	5.98	6.57	9.70

[a] Conditions: [complex] = 1 mM; $[S]_T$ = 0.01 M; temp, 25 °C.

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Registry No. *cis*-$[Co(en)_2(H_2O)_2]^{3+}$, 21247-59-6; SO_3^{2-}, 14265-45-3; SO_2, 7446-09-5; *cis*-$[Co(en)_2(H_2O)(OSO_2)]^+$, 93254-95-6.

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(16) Hughes, R. G.; Endicott, J. F.; Hoffman, M. Z.; House, D. A. *J. Chem. Educ.* **1969**, *46*, 440.

(17) In the case of tren complex,[4] above pH 7 internal redox is no longer observable, but further sulfite substitution occurs to yield a very stable bis(sulfito) end product. In the present system, the rate of cis → trans isomerization increases at pH ≥5 to such an extent as to make it exceed the rate of redox. Thus, at pH 6.1 the rate of cis to trans conversion of the major form of the reactant, $[Co(en)_2(OH)(OH_2)]^{2+}$, is nearly 3 times greater at 25 °C than the apparent rate of redox decomposition (see Table V and ref 5).