transition region but, in the energy region higher than about 4.1 μm^{-1}, exhibit strongly positive optical activity because of asymmetric carbons of L-(+)-tartrate ion contained in the complexes.

The CD spectra of the L-tartrato and oxalato complexes[4] are also similar to each other. Both complexes show one dominant CD band in the first absorption band region (at about 2.0 μm^{-1}) and the weak CD band in the second absorption band region (at about 2.5 μm^{-1}). On the basis of the sign of the dominant CD peak in the first absorption band region, absolute configuration of L-tartrato complexes can be assigned. Each $(-)_D$ isomer with a negative major CD peak is assigned to Δ configuration and each $(+)_D$ isomer with a positive major CD peak to Λ configuration (Figures 1 and 2).

On the other hand, according to the exciton theory it can be predicted that bis(phen) or bis(bpy) complexes show a positive and a negative CD band from the lower frequency side in the ligand π–π^* transition region for Λ configuration and the reverse holds for Δ configuration.[9-11] The exciton CD bands are observed here at about 3.7 μm^{-1} for the phen complexes and at about 3.3 μm^{-1} for the bpy complexes. Thus, from the prediction of the exciton theory it can be concluded that $(+)_D$ isomers should be assigned to Λ configuration and $(-)_D$ isomers to Δ configuration for $[Cr(L\text{-tart})(phen\ or\ bpy)_2]^+$, being consistent with the assignment based on the major CD component in the first absorption band region.

On the other hand, although $(-)_D$-$[Cr(ox)(bpy)_2]^+$ shows a minor positive CD peak ($\Delta\epsilon$ +0.055 at 1.792 μm^{-1}) and a major negative CD peak ($\Delta\epsilon$ −1.274 at 2.055 μm^{-1}) in the first absorption band and shows two intense CD peaks of opposite sign ($\Delta\epsilon$ −17.63 at 3.226 μm^{-1} and $\Delta\epsilon$ +7.12 at 3.435 μm^{-1}) in the ligand π–π^* transition region, ref 4 attributes the CD spectrum obtained for $(-)_D$-$[Cr(ox)(bpy)_2]^+$ to Λ configuration.[4] However, on the basis of the similar CD spectra between $(-)_D$-$[Cr(ox)(bpy)_2]^+$ and $(-)_D$-$[Cr(L\text{-tart})(bpy)_2]^+$ and of the elution order for the diastereoisomers of the L-tartratobis(phen or bpy)chromium(III) and -cobalt(III) complexes in our study, $(-)_D$-$[Cr(ox)(bpy)_2]^+$ has the same absolute configuration as $(-)_D$-$[Cr(L\text{-tart})(phen\ or\ bpy)_2]^+$ and should be assigned to the Δ configuration.

The elution curves of the chromium(III) complexes were similar to those of the corresponding cobalt(III) complexes[2] for both the phen and the bpy systems and the elution order of the diastereoisomers was also the same as that observed for the cobalt(III) complexes; that is, the first eluted band was the $(-)_D$-Δ isomer and the second band was the $(+)_D$-Λ isomer. From the area of the band in the elution curves and the molar extinction coefficient, the formation ratios of the isomers were evaluated.

The value Δ-L:Λ-L = 1.2:1.0 was obtained for the phen complexes and the value Δ-L:Λ-L = 1.3:1.0 for the bpy complexes. These formation ratios (Δ-L:Λ-L) of the chromium(III) complexes are quite different from those of the corresponding cobalt(III) complexes: Δ-L > Λ-L for Cr(III) complexes, whereas Δ-L < Λ-L for Co(III) complexes. This fact may suggest that the mechanism of ligand substitution reaction differs for the two systems, even though it should be related in part to the difference of the reaction conditions (temperature and reaction time).

Acknowledgment. The author is grateful to Professor Y. Yamamoto of Hiroshima University for helpful discussions and encouragement throughout this work.

Registry No. $(-)_D$-Δ-$[Cr(L\text{-tart})(phen)_2]ClO_4$, 61812-71-3; $(+)_D$-Λ-$[Cr(L\text{-tart})(phen)_2]ClO_4$, 61849-37-4; $(-)_D$-Δ-$[Cr(L\text{-tart})(bpy)_2]ClO_4$, 61812-73-5; $(+)_D$-Λ-$[Cr(L\text{-tart})(bpy)_2]ClO_4$, 61849-39-6; $[CrCl_2(phen)_2]Cl$, 31282-15-2; $[CrCl_2(bpy)_2]Cl$, 26154-79-0.

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Influence of Coordinated Thioethers in the Iron(II) Reduction of *cis*-Dibromo(1,8-diamino-3,6-dithiaoctane)cobalt(III) Perchlorate

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Received October 12, 1976 AIC60742A

The initial observations concerning the role of sulfur on rate enhancement,[1-3] kinetic trans effects,[4-6] and electronic ground state modifications[7] are the results of model system investigations using transition metal complexes containing coordinated sulfur.

A comparison of rate constants for reduction of cobalt(III) complexes containing halide or pseudohalide ions positioned cis and trans to nitrogen donors with rate constants for cobalt(III) complexes having thioether donors cis and/or trans to possible bridging groups demonstrates the unique influence of sulfur.[2,3] A similar comparison using reduction potentials for Cu(II)/Cu(I) chelates of cyclic and open chain polythiaethers and aminothiaethers further suggests that the enhanced reducibility of the complexes is not dependent on increased chelation or coordinative distortion.[8]

This report deals with the rate and mechanism for the iron(II) reduction of *s-cis*-dibromo(1,8-diamino-3,6-dithiaoctane)cobalt(III) perchlorate, *s-cis*-$[Co(eee)Br_2]ClO_4$, in aqueous perchloric acid.

Experimental Section

Preparation of *s-cis*-$[Co(eee)Br_2]ClO_4$. This complex was prepared as the bromide salt following literature procedures[9,10] and precipitated as the perchlorate salt from aqueous $LiClO_4$–$HClO_4$ media, λ_{max} (ϵ) 625.5 nm (ϵ 377). Prior to conversion to the perchlorate salt a portion of it was converted to *s-cis*-$Co(eee)Cl_2^+$ and *s-cis*-$Co(eee)(NO_2)_2^+$. The visible, ultraviolet, and infrared absorption spectra were found to be identical with those of authentic cis isomers previously prepared. This was to ensure that the complex reported in this study was indeed the cis isomer and not a trans species.

Materials. Stock solutions of $Fe(ClO_4)_2$, $LiClO_4$, and $HClO_4$ were prepared and standardized as reported earlier.[3]

Kinetic Measurements. The complex was dissolved in 0.098 M $HClO_4$; then precalculated volumes of complex, $HClO_4$, $LiClO_4$, and H_2O were delivered via syringe techniques into a 5.0-cm spectrophotometer cell. After temperature equilibrium was established, the iron(II) solution was added and the cell was shaken and placed in the Cary 14 temperature controlled cell holder. The reaction was followed by a decrease in absorbance at 625.5 nm as a function of time for over 10 half-lives. In all experiments the iron(II) concentration was in excess with respect to cobalt(III) and pseudo-first-order rate constants were obtained from computer calculated least-squares slopes of log $(D_t - D_\infty)$ vs. time plots. The plots were linear over 95% of reaction and did not exhibit signs of competitive reactions, as would be expected if the complex was not a pure single entity. All runs were performed in duplicate or triplicate if the average deviation of the

Table I. Rate Constants and Experimental Conditions for the *s-cis*-Co(eee)Br_2^+ + Fe^{2+} Reaction[a,b]

T, °C	$[H_3O^+]$, M	[Co(III)] × 10^4, M	[Fe(II)] × 10^2, M	k_t × 10^2, M^{-1} s^{-1}
25.0	0.20	4.0	5.5	9.59
	0.25			9.67
	0.30			9.25
	0.35			9.66
	0.40			9.96
	0.45			9.49
	0.50			9.82
	0.60			9.31
	0.70			9.87
25.0	0.40	4.0	2.0	9.48
			4.0	9.35
			5.5	9.96
			6.0	9.16
			7.0	9.48
			8.0	9.70
25.0	0.40	1.0	5.5	8.92
		2.0		9.45
		3.0		10.6
17.8	0.40	4.0	5.5	5.27
32.8				15.0
33.4				16.7

[a] Total $[ClO_4^-]$ = 1.00 M, maintained with aqueous $LiClO_4$.
[b] At 25 °C k_t = 0.0969 M^{-1} s^{-1} with a standard deviation of ±0.004 M^{-1} s^{-1}.

determined rate constants was 4% or greater.

Results and Discussion

The reaction between iron(II) and *s-cis*-Co(eee)Br_2^+ was followed kinetically under a variety of controlled conditions of total perchlorate ion, perchloric acid, complex, and iron(II) concentrations and temperature. The results of this investigation are summarized in Table I where k_t is defined as $k_{obsd}/[Fe(II)]$. Examination of columns 2 and 5 demonstrates that the transition state for the reduction process is independent of hydrogen ion (or hydroxide) over the range $0.20 < H_3O^+ < 0.70$ M. The first-order kinetic dependence of the reaction on complex and iron(II) concentration is presented in columns 3, 4, and 5. These data are consistent with a simple mixed second-order rate law of the form

$$\frac{-d[Co(eee)Br_2^+]}{dt} = k[Fe(II)][Co(eee)Br_2^+] \qquad (1)$$

corresponding to the chemical process

$$s\text{-}cis\text{-}Co(eee)Br_2^+ + Fe^{2+} \xrightarrow[k_{obsd}]{H_3O^+} Co^{2+} + Fe^{3+} + 2Br^- + eeeH_2^{2+} \qquad (2)$$

From these data, we calculate the best numerical value of k_t to be 0.097 ± 0.004 M^{-1} s^{-1} at 25.0 °C and a total perchlorate concentration of 1.00 M. The reaction was examined at several different temperatures: 17.8, 25.0, 32.8, and 33.4 °C. A plot of ln k_t/T vs. $1/T$ gives a computer calculated slope which, when used with transition state theory, gives thermodynamic parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 12.1 ± 0.93 kcal/mol and −22.9 ± 3.1 eu, respectively. The error limits given are in standard deviations.

Earlier studies of the Co(eee)Cl_2^+–Fe^{2+} reduction process were performed in $NaClO_4$–$HClO_4$ medium. Because the great majority of Fe(II)–Co(III) kinetic studies are examined in $LiClO_4$–$HClO_4$ with data reported at 25 °C and $\sum[ClO_4^-]$ = 1.0 M, several recent experiments were conducted to update our earlier work.[3] These results are presented in Table II. From the above data in $LiClO_4$–$HClO_4$ medium, we calculate the thermodynamic parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ to have the values of 10.4 ± 0.80 kcal/mol and −22.6 ± 2.7 eu, respectively. A recalculation using our earlier data in $NaClO_4$–$HClO_4$ gives $\Delta H^\ddagger$ = 9.3 ± 0.4 kcal/mol and $\Delta S^\ddagger$ = −27.1 ± 1.1 eu.

Table II. Temperature Dependence on k_t for the Co(eee)Cl_2^+-Fe^{2+} Reaction in $LiClO_4$-$HClO_4$[a]

Temp, °C	$k_{obsd}/[Fe(II)] = k_t$, M^{-1} s^{-1}	Temp, °C	$k_{obsd}/[Fe(II)] = k_t$, M^{-1} s^{-1}
25.0	1.66 ± 0.03	32.6	2.43 ± 0.08
18.0	0.99 ± 0.03	33.7	2.60 ± 0.08
18.4	0.99 ± 0.03		

[a] [Co(III)] = 7.8 × 10^{-4} M; $[Fe^{2+}]$ = 0.01 M; $[H_3O^+]$ = 0.10 M; $\Sigma[ClO_4]$ = 1.00 M, maintained with $LiClO_4$-$HClO_4$.

Table III. Rate Constants for the Fe(II) Reduction of Several Bromo- and Chlorocobalt(III) Complexes

Complex	k,[a] M^{-1} s^{-1} $X^- = Cl^-$	$X^- = Br^-$	Ref
s-cis-Co(eee)X_2^+	1.66[a]	9.69 × 10^{-2}	This work
$Co(NH_3)_4NH_3X^{2+}$	1.35 × 10^{-3}	8.89 × 10^{-4}	11, 14
cis-$Co(en)_2NH_3X^{2+}$	1.8 × 10^{-5}	6.1 × 10^{-6}	11, 12
cis-$Co(en)_2H_2OX^{2+}$	4.5 × 10^{-4}	2.8 × 10^{-4}	11, 12
trans-$Co(en)_2X_2^+$	3.2 × 10^{-2}	1.85 × 10^{-2}	11, 12
trans-$Co(en)_2H_2OX^{2+}$	2.4 × 10^{-1}	9.41 × 10^{-2}	11, 12

[a] 25 °C, $LiClO_4$-$HClO_4$, $\Sigma[ClO_4^-]$ = 1.0 M.

The most comprehensive study available on the Fe(II) reduction of *cis*- and *trans*-bromocobalt(III) complexes is due to the researches of Linck.[11] Reports on the reduction of *cis*-$Co(NH_3)_4Br_2^+$, *cis*-$Co(en)_2Br_2^+$, and *s-cis*-Co(trien)Br_2^+, although desirable for a comparison with our work, are not available because their rates of aquation and/or isomerization are considerably greater than their rates of reduction by Fe(II). Table III summarizes the rate coefficients determined for the Fe(II) reduction of several pertinent bromo- and chlorocobalt(III) complexes. The similarity in the Fe(II) reactivity patterns with Co(III)–Br^- systems and with the Co(III)–Cl^- systems, suggests that the mechanism for the *s-cis*-(Co(eee)Br_2^+–Fe^{2+} reaction is also of the inner-sphere type. The background and evidence in support of this basic assumption have been reported earlier.[11-13]

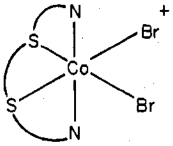
The general conclusions one can derive from Table II are: (1) chloro complexes react more rapidly than their bromo counterparts; (2) trans geometries are more reactive than cis geometries; (3) the presence of aqua ligands either cis or trans to a potential bridging group enhances the reduction rate with Fe(II); (4) by increasing chelation, as in substituting ethylenediamine for ammonia, the rate of both chloro and bromo complexes is reduced by a factor of about 100. These observations are not new;[11,12] however, the rate coefficients determined in the present work for both *s-cis*-Co(eee)Cl_2^+ and *s-cis*-Co(eee)Br_2^+ provide an interesting contrast.

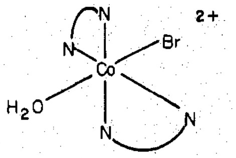
The observed reactivity patterns of the ammine and ethylenediamine complexes are rationalized in terms of the relative crystal field strength of ligands trans to the inner-sphere bridging ligand coupled with the ability of the bridging ligand and its trans component to simultaneously stretch, moving away from the Co(III) center. Hydrolytic ligands such as H_2O and N_3H^+ can be solvent assisted as they move from their coordinated positions into the bulk solvent. As reviewed by Linck[15] and Earley[16] this simplistic physical picture affords a lowering of the d_{z^2} acceptor orbital energy on the oxidant. The net result is an enhanced rate of reduction in systems where the trans ligand has a weak crystal field strength or can be assisted into the bulk solvent by its physical nature.

That *s-cis*-Co(eee)Br_2^+ reacts faster than *trans*-$Co(en)_2H_2OBr^{2+}$ is surprising. The crystal field strength of H_2O is greater than that of Br^-, yet the average CFS along the

Table IV. Activation Parameters for the Iron(II) Reduction of Some Bromo- and Chlorocobalt(III) Complexes

Complex	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol	Ref
cis-$[Co(eee)Br_2]^+$	12.1	−22.9	18.9	This work
cis-$[Co(eee)Cl_2]^+$	10.5	−22.6	17.2	This work
$[Co(NH_3)_5Br]^{2+}$	15.5	−20.14	21.6	11
$[Co(NH_3)_5Cl]^{2+}$	12.5	−30	21.5	14
cis-$[Co(en)_2(NH_3)Br]^{2+}$	17.6	−23.2	24.5	11
cis-$[Co(en)_2(OH_2)Br]^{2+}$	15.4	−23.2	22.3	11





pertinent axis is fairly weak. Also H_2O can diffuse with solvent assistance into the bulk solvent quite readily. These factors lower the e_g acceptor orbital on Co(III) and a rapid reduction of *trans*-$Co(en)_2H_2OBr^{2+}$ is observed. In the case of *s-cis*-$Co(eee)Br_2^+$, the axis at which reaction occurs is also influenced by a weaker average crystal field strength due to Br^- and R–S–R donor. The problem arises in our ability to envision the movement of the R–S–R donors away from the Co(III) center and into the bulk solvent, prior to electron transfer. Molecular models and stereochemical studies[9,10] strongly suggest that the chelate ring conformations are quite rigid and that appreciable mobility of the R–S–R donor is lacking. Furthermore, the effect of increased chelation tends to slow down reduction processes between Fe(II) and Co(III) complexes.[12]

We believe the reason for the marked increase in the rate coefficient for the reduction of *s-cis*-$Co(eee)Br_2^+$ is due to the presence and interaction of the thioether donor atoms in the ligand eee. A similar significant rate increase has previously been observed for the corresponding dichloro-[2] and oxalatocobalt(III)[3] complexes containing eee. The explanation we advance for this observation is that the empty low-lying d orbitals of sulfur interact with the Co(III) molecular orbitals promoting significant M→L back-bonding within the complex. This Co(III)–S association lowers the oxidant's acceptor orbital energy, facilitating transfer of an electron from the Fe(II) reductant to the oxidant. Experimentally one observes an enhanced overall rate of reduction for the eee series of compounds as compared to ammine and ethylenediamine complexes.

This concept is further strengthened by the recent work of Rorabacher and co-workers,[8] who demonstrate that thiaether-containing ligands stablize the lower oxidation state in complexes of the type $Cu^{I}eee^+$ as opposed to $Cu^{II}eee^{2+}$. In contrast, the presence of NH_2 and/or HN< donors within a linear tetradentate ligand design creates the opposite effect, stabilizing the metal in a higher oxidation state and destabilizing the lower oxidation state.

Bifano and Linck[17] suggest that the parameter most likely to influence the energy of the acceptor orbital in Fe(II)–Co(III) systems is the σ component of the bonding strength for the nonbridging ligands. The smaller the σ contribution, the more rapid the observed reduction rate. The σ component concept can be invoked as a possible explanation in the eee series; however, is it in reality substantially different from Orgel's original crystal field strength (CFS) suggestions? Are not CFS and σ donor strength one in the same when applied to the above problem?

It is interesting to note that the point one obtains by plotting log k_{Br^-} vs. log k_{Cl^-} for *s-cis*-$Co(eee)Br_2^+$ and *s-cis*-$Co(eee)Cl_2^+$ does not fall within the proximity of the line Linck obtained for a series of ammine and ethylenediamine bromo- and chlorocobalt(III) complexes reacting with Fe(II).[11] The established reactivity pattern, $k_{Cl^-} > k_{Br^-}$, however, is mantained in the eee series.

The high reactivity of *s-cis*-$Co(eee)Br_2^+$ and *s-cis*-$Co(eee)Cl_2^+$ when compared with the traditional amine and ethylenediamine complexes is caused primarily by the change in $\Delta H^{\ddagger}$. Table IV presents the activation parameters for a series of related complexes. The data are consistent with the observations and conclusions of Linck[11] and the quantitative analysis of Hush[18] that in this comparison the enthalpy of activation reflects a perturbution of the Co(III) center by the nonbridging ligands and is primarily electronic in nature, reducing the energy of the acceptor orbital of the oxidant.

Reports concerning the kinetic and electronic influences exerted by coordinated sulfur are quite limited. Future work in this laboratory is designed to examine more closely the electronic role of coordinated sulfur ligands.

Registry No. *s-cis*-$Co(eee)Br_2^+$, 46135-49-3; *s-cis*-$Co(eee)Cl_2^+$, 32594-33-5; Fe^{2+}, 15438-31-0.

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Occurrence of Corundum-Type Indium(III) Oxide under Ambient Conditions

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Received November 23, 1976 AIC608542

At room temperature and ambient pressure, the Mn_2O_3-type modification (space group *Ia*3) is the stable form of In_2O_3 (In_2O_3(I)). The unit cell is derived from a distorted fluorite structure with one-fourth of the anion sites being unoccupied.[2]

The existence of a high-temperature, high-pressure rhombohedral modification of In_2O_3 (In_2O_3(II)) with the corundum structure (space group $R\bar{3}c$) has been reported in the literature.[3-5] This phase is 2.5% denser than cubic In_2O_3(I); the cation–anion distances are nearly the same but the anion packing is somewhat distorted from a close-packed hexagonal arrangement without vacancies, the distortion, however, being smaller than that of In_2O_3(I).[5] Shannon obtained small crystals of In_2O_3(II) at 1250 °C and 65 kbars,[3] and Christensen et al.[4] observed the occurrence of In_2O_3(II)

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