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Kinetics and Mechanism for the Reduction of the Oxalato(1,8-diamino-3,6-dithiaoctane)cobalt(III) Ion by Iron(II)

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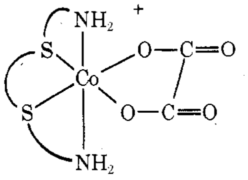
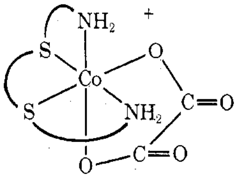
Data are presented for the iron(II) reduction of *s-cis*-oxalato(1,8-diamino-3,6-dithiaoctane)cobalt(III) ion, $Co(eee)C_2O_4^+$. At 25° and 1.0 M total ClO_4^-, the second-order rate constant k_t defined by the rate law $-d[Co(eee)C_2O_4^+]/dt = k_t[Co(eee)C_2O_4^+][Fe(II)]$ is $1.65 \pm 0.05\ M^{-1}\ sec^{-1}$ with activation parameters $\Delta H^{\ddagger} = +10.7 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -21.5 \pm 0.8$ eu in $HClO_4$–$LiClO_4$ media. These results are discussed and contrasted with analogous ammine and bis(ethylenediamine)oxalatocobalt(III) ion reductions by iron(II). The marked 10^3 increase in reduction rate in the present system illustrates a dramatic nonbridging ligand effect due to placing thioether functions trans to potential bridging ligands.

Introduction

Our interest in the reduction of diacidocobalt(III) complexes by iron(II) involves the role of stereochemistry and the selective placement of coordinated thioether groups trans to bridging ligands. We wish to report here the reduction kinetics for the oxalato(1,8-diamino-3,6-dithiaoctane)cobalt(III) ion, $Co(eee)C_2O_4^+$. This complex can theoretically exist as two unique geometrical isomers, a symmetrical cis and an unsymmetrical cis arrangement as illustrated below. To date all synthetic investigations demonstrate sole isolation of only the symmetrical cis isomer.[3] In distinct contrast to the slow iron(II) reductions of acidopentaamine- and diacidotetraaminecobalt(III) ions, the iron(II) reduction of $Co(eee)C_2O_4^+$ is very rapid, being 3.9×10^3 times more reactive than the tetraamine analog.[4]



s-cis



u-cis

The influence of thioether donor groups positioned trans to chloride bridging atoms has been demonstrated in the reduction of *s-cis*-$Co(eee)Cl_2^+$ by iron(II).[5] Recent reports concerning the attack of chromium(II) on sulfur bound to cobalt(III) accent the importance of redox work with sulfur-containing ligands.[6,7]

Experimental Section

Preparation of $[Co(eee)C_2O_4]ClO_4 \cdot H_2O$.—Two grams of *s-cis*-$[Co(eee)Cl_2]Cl$, prepared as described in the literature,[3] was treated with 1.02 g of $Li_2C_2O_4$ in 20 ml of water. The mixture was heated to 50° on a hot plate until the blue color characteristic of the dichloro salt was replaced by the deep red coloration of the oxalato complex.

Immediately upon filtering, 10 ml of a saturated aqueous solution of $NaClO_4$ was added, whereupon cooling produced deep red needles. These were collected by filtration and washed with cold water, ethanol, acetone, and ether, yield 1.80 g. *Anal.* Calcd for $[Co(C_6H_{16}N_2S_2)C_2O_4]ClO_4 \cdot H_2O$: C, 21.62; H, 4.05; N, 6.30. Found: C, 21.67; H, 4.11; N, 6.31. Recrystallization of the needles from warm water produced a mixture of distinct platelets and needles which were collected and treated as stated above. Samples for kinetic studies were carefully recrystallized three additional times to produce pure plates (see Discussion). *Anal.* Found: C, 21.51; H, 3.99; N, 6.29.

Analyses were determined by Galbraith Laboratories, Knoxville, Tenn.

Materials.—Stock solutions of iron(II) perchlorate were prepared by dissolving reagent grade ferrous perchlorate (G. F. Smith) in 0.100 M $HClO_4$ under nitrogen. The iron(II) concentration was determined by titration with standard potassium dichromate using diphenylaminesulfonate as the indicator.[8] The iron(III) concentration was determined by reducing all iron(III) present to iron(II) with excess stannous chloride and then redetermining the total iron(II)[9] concentration as given above, the difference being equal to [Fe(III)]. In all cases the iron(III) concentration was less than 3% of the total iron.

Total perchlorate concentration was determined gravimetrically as tetraphenylarsonium perchlorate, and by anion-exchange techniques. Total acid was determined by passing an aliquot of the iron(II) solution through a Dowex 50-X8 ion-exchange column in the hydrogen form and titrating the eluent with standard sodium hydroxide using phenolphthalein as the indicator. The concentration of acid in the solution was determined by difference from a knowledge of Fe(II) and Fe(III) concentrations. Acid concentration was also determined from a knowledge of the total perchlorate, Fe(II) and Fe(III) concentrations and was found in excellent agreement with the above method.

The total perchlorate concentration for kinetic runs was adjusted using precalculated volumes of standardized 5.0 M $NaClO_4$ or 2.0 M $LiClO_4$ solution which was prepared by neutralizing Na_2CO_3 or Li_2CO_3, respectively, with standard $HClO_4$.

Kinetic Measurements.—The rapid reactions required that the experiments be performed by delivering all the reagent solutions (complex, acid, sodium or lithium perchlorate) except that of iron(II) into the spectrophotometer cell (5.0 or 10.0 cm). The cell was placed in a constant-temperature bath and allowed to equilibrate for a period of 15–20 min. The thermostated iron(II) solution was then added to the cell by syringe techniques. At this point, the cell was capped, shaken two or three times, and then quickly placed in the thermostated cell holder of the Cary 14 spectrophotometer. In this manner, the first optical density measurements were obtained within 30 sec. The optical density corresponding to complete reaction was measured after 8–10 half-lives.

In all experiments the iron(II) was in excess with respect to the cobalt(III), and pseudo-first-order rate constants were obtained from computer calculated least-squares slopes of plots of log $(D_t - D_\infty)$ *vs.* time. The optical densities at time t and after the reaction is complete are D_t and D_∞, respectively. In all cases such plots were linear for 90–95% reaction. All data points

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[1] National Science Foundation Undergraduate Research Participant, summer, 1970.

[2] NSF-URP Visiting Participant from University of North Carolina at Charlotte, summer, 1971.

[3] J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1563, 1572 (1969). eee = $NH_2CH_2CH_2SCH_2CH_2SCH_2CH_2NH_2$.

[4] C. Hwang and A. Haim, *ibid.*, **9**, 500 (1970).

[5] J. H. Worrell and T. A. Jackman, *J. Amer. Chem. Soc.*, **93**, 1044 (1971).

[6] R. H. Lane and L. E. Bennett, *ibid.*, **92**, 1089 (1970).

[7] C. Shea and A. Haim, *ibid.*, **93**, 3055 (1971).

[8] P. Benson and A. Haim, *ibid.*, **87**, 3826 (1965).

[9] W. J. Blaedel and V. W. Meloche, "Elementary Quantitative Analysis," 2nd ed, Harper and Row, New York, N. Y., 1963, p 473.

are an average of at least three individual determinations of k_t at the specified conditions.

Results

The kinetic data pertinent to the reduction of the $Co(eee)C_2O_4^+$ ion by iron(II) in aqueous solution is presented in Tables I, II, and III. The values of the second-order rate constant, k_t, which appear in the last column of each table, were calculated from the relationship $k_t = k_m/[Fe(II)]$ where k_m is the measured pseudo-first-order rate constant. From Table I it can be seen that in $LiClO_4$–$HClO_4$ media, the value of k_t is constant when the [Co(III)], $[H_3O^+]$, and [Fe(II)] concentrations ranges are (0.5–2.5) × 10^{-3} *M*, 0.10–0.95 *M*, and 0.015–0.030 *M*, respectively. These data are consistent with a simple mixed second-order rate law of the form (1).

TABLE I

KINETIC DATA FOR THE REDUCTION OF $Co(eee)C_2O_4^+$ BY IRON(II) IN $LiClO_4$–$HClO_4$ MEDIA[a]

[Fe(II)], *M*	$[H_3O^+]$, *M*	Temp, °C	k_t, M^{-1} sec^{-1}
0.015–0.02	0.20	25.0	1.61 ± 0.05
0.02–0.03	0.40	25.0	1.63 ± 0.05
0.02	0.60	25.0	1.64 ± 0.05
0.02	0.80	25.0	1.67 ± 0.05
0.02	0.95	25.0	1.71 ± 0.05
			Av 1.65 ± 0.05
0.03	0.50–0.80	15.0	0.88 ± 0.03
0.02	0.60–0.80	20.0	1.22 ± 0.03
0.02	0.60	30.0	2.33 ± 0.03
0.02	0.60	35.0	3.26 ± 0.09

[a] [Co(III)] = (0.5–2.5) × 10^{-3} *M*, $\Sigma[ClO_4^-]$ = 1.0 *M*, plate form of crystals, $\Delta H^{\ddagger}$ = 10.7 kcal/mol, $\Delta S^{\ddagger}$ = −21.5 eu.

$$\frac{-d[Co(eee)C_2O_4^+]}{dt} = k_t[Co(eee)C_2O_4^+][Fe(II)] \quad (1)$$

Thermodynamic activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from plots of log k_t/T *vs.* $1/T$ using a computer least-squares program and transition-state theory. Based on the determination of k_t at five different temperatures over the interval 15–35°, we find $\Delta H^{\ddagger}$ = 10.7 ± 0.3 kcal/mol and $\Delta S^{\ddagger}$ = −21.5 ± 0.8 cal/mol deg in $LiClO_4$–$HClO_4$ media.

When sodium perchlorate is substituted for lithium perchlorate as the background electrolyte, an unusual variation in the value of k_t is observed. Table II presents the values of k_t at 25° as a function of acid and sodium ion concentration. Simultaneously as the hydronium ion concentration increases, sodium ion concentration decreases. Figure 1 shows that this change is accompanied by a 36% increase in the value of k_t from 1.17 M^{-1} sec^{-1} at 0.10 *M* H_3O^+ (0.84 *M* Na^+) to 1.60 M^{-1} sec^{-1} at 0.95 *M* H_3O^+ (0.01 *M* Na^+). Although a plot of $[H_3O^+]$ *vs.* k_t is linear, we choose not to consider this trend as a chemical manifestation of two parallel paths for reduction, one being acid independent and one acid dependent. The work in aqueous $LiClO_4$–$HClO_4$ is clearly acid independent (Tables I and III). Admittedly the observed 36% rate change is modest and is not in the range of generally accepted medium effects for other oxidation–reduction reactions.[10,11] Extensive repetitive work in our laboratories using $NaClO_4$, $LiClO_4$, $Mg(ClO_4)_2$, and $Ca(ClO_4)_2$ as background electrolytes has not suggested a possible cause for the moderate rate change observed for $NaClO_4$–$HClO_4$ media. At present, these results demonstrate that rate data acquired using $LiClO_4$–$HClO_4$ media are more readily interpretable and that acid dependences observed in $NaClO_4$–$HClO_4$ media for molecules containing two adjacent oxygen functions should be reexamined in $LiClO_4$–$HClO_4$ media.[12]

TABLE II

KINETICS OF THE $Co(eee)C_2O_4^+$–Fe^{2+} REACTION IN $NaClO_4$–$HClO_4$ MEDIA[a]

No. individual runs	10^3 × [Co(III)], *M*	[Fe(II)], *M*	$[H_3O^+]$, *M*	$[Na^+]$, *M*	k_t, M^{-1} sec^{-1}
16	1.03–2.00	0.015–0.030	0.10	0.84–0.87	1.17 ± 0.04
6	1.01	0.02	0.20	0.76	1.19 ± 0.03
6			0.40	0.56	1.29 ± 0.03
8			0.60	0.36	1.41 ± 0.04
6			0.80	0.16	1.54 ± 0.04
6			0.95	0.01	1.60 ± 0.05

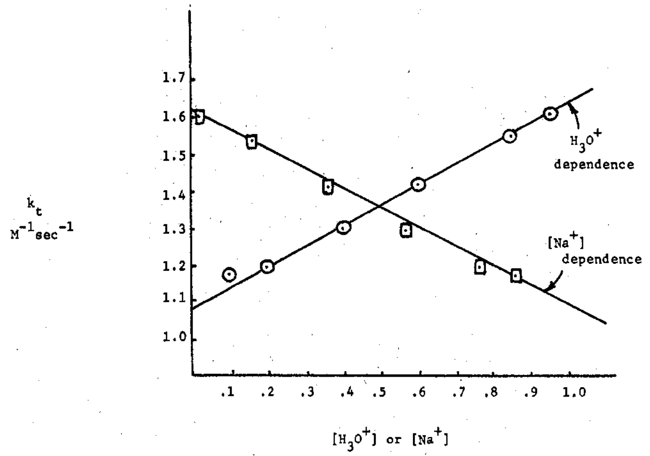

Figure 1.—Effect of $[H_3O^+]$ or $[Na^+]$ on the $CO(eee)C_2O_4^+$–Fe^{2+} reaction in $NaClO_4$–$HClO_4$ media.

The compound $[Co(eee)C_2O_4]ClO_4 \cdot H_2O$ was isolated in two distinct crystalline forms. The possible existence of two geometrical isomers for $Co(eee)C_2O_4^+$ in addition to the analytical data supporting the compound's chemical formulation as a monohydrate required that kinetic data be collected for both isolated crystalline forms, needles and plates. Table III demonstrates the acid independence for the Fe(II) reduction of both crystalline forms of *s-cis*-$Co(eee)C_2O_4^+$ at 22°. Linearity of $(D_t - D_\infty)$ *vs.* time plots in addition to the same average rate constant (1.32 ± 0.02 M^{-1} sec^{-1}) for both plate and needle forms support our premise that we are dealing with a single geometric isomer, the s-cis form.

TABLE III

ACID DEPENDENCE FOR THE TWO CRYSTALLINE FORMS OF $Co(eee)C_2O_4^+$ ON REACTION WITH Fe(II)[a]

	Needle form	Plate form
$[H_3O^+]$, *M*	k_t, M^{-1} sec^{-1}	k_t, M^{-1} sec^{-1}
0.20	1.29 ± 0.03	1.29 ± 0.03
0.40	1.35 ± 0.03	1.32 ± 0.03
0.60	1.34 ± 0.03	1.29 ± 0.03
0.80	1.35 ± 0.03	1.35 ± 0.03

[a] [Co(III)] = 1 × 10^{-3} *M*, [Fe(II)] = 0.02 *M*; $\Sigma[ClO_4^-]$ = 1.00 *M*, *T* = 22.0°, $LiClO_4$–$HClO_4$ media.

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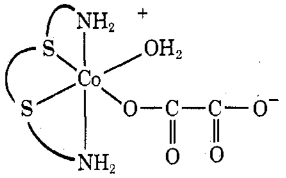
[10] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

[11] R. D. Butler and H. Taube, *J. Amer. Chem. Soc.*, **87**, 5597 (1965).

[12] See for example R. T. M. Fraser, *ibid.*, **85**, 1747 (1963); B. Grossman and A. Haim, *ibid.*, **93**, 6490 (1971).

Discussion

Complex Geometry.—Our observation that two unique crystalline forms could be isolated, each possessing identical stoichiometries consistent with the formulation $[Co(eee)C_2O_4]ClO_4 \cdot H_2O$, raises several questions. First, are these two crystalline forms a manifestation of the s-cis and u-cis geometric isomers or is one form, either plates or needles, possibly an aquo-oxalato complex in which the oxalate group is coordinated in a monodentate fashion as illustrated below? A number of experiments were performed to clarify these issues.



Electronic absorption spectra for both plates and needles were identical, having a single symmetrical d–d transition, $^1A_{1g} \rightarrow {}^1T_{1g}$, maximum at 5175 Å and a shoulder positioned at 3800 Å on the tail of an intense charge-transfer band located in the ultraviolet region. Three separate molar extinction coefficient determinations were made on each crystalline solid; $\epsilon_{5175} = 222.7 \pm 3$ for plates and $\epsilon_{5175} = 218.6 \pm 3$ for the needles. Infrared vibrational spectra taken in Nujol mulls were identical. Both crystalline forms presented exactly the same display in both position and relative peak intensity throughout the range 4000–200 cm^{-1}. Two strong absorption bands at 3550 and 3615 cm^{-1} are suggestive of lattice water hydrogen bonded to either oxalate or perchlorate oxygen atoms. The complex $Co(eee)(H_2O)_2{}^{3+}$ reacts rapidly with $NO_2{}^-$ to produce $Co(eee)(NO_2)_2{}^+$. A similar facile reaction would be expected to occur, $NO_2{}^-$ replacing H_2O, in the aquo-oxalato complex $Co(eee)(H_2O)C_2O_4{}^+$. Such a test proved negative with both plates and needles. Electronic absorption spectra were found to be insensitive to changes in $[H_3O^+]$ in the range 0.1–1.0 M $HClO_4$, being indicative of bidentate oxalate on the complex. These observations are consistent with our assumption that both crystalline modifications have the same complex geometry, presumably the s-cis form in which the oxalate group functions as a bidentate chelate. The data in Table III demonstrate that the two crystalline forms are kinetically indistinguishable.

Reduction of Complex.—The second-order rate law given by (1) suggests that the rate-determining step of the reduction process in $LiClO_4$–$HClO_4$ media involves one hydrated iron(II) and one $Co(eee)C_2O_4{}^+$ ion (2)

$$(H_2O)_6Fe^{II} + Co(eee)C_2O_4{}^+ \xrightarrow{H_3O^+} Co(II) + Fe(III) + eeeH_2{}^{2+} + H_2C_2O_4 \quad (2)$$

but does not distinguish between an inner-sphere or outer-sphere mechanism. The rate of equilibration for reaction 3 is very rapid compared to the rates of most oxidation–reduction reactions involving iron(II) and a cobalt(III) complex, and therefore the primary reduction product usually cannot be identified. Haim and Sutin have explored the generality of inner-sphere mechanisms for cobalt(III)–iron(II) reactions where the bridging ligands are chloride, azide, and oxalate.[13] Flow techniques allowed the establishment of an inner-sphere mechanism in these cases. Although the tendency of iron(II) to react by an inner-sphere mechanism is not well established beyond the above work, it is usually assumed.[4,5,8,14,15] Considering the established $Co(C_2O_4)_3{}^{3-}$–Fe(II) reaction mechanism[13] and the rapidity of the $Co(eee)C_2O_4{}^+$–Fe(II) reduction, we are inclined to favor a bridged activated complex for the present work.

$$2H^+ + FeC_2O_4{}^+ \rightleftharpoons Fe^{3+} + H_2C_2O_4 \quad (3)$$

Reduction in $NaClO_4$–$HClO_4$ Media.—The marked decrease in reduction rate with increasing $[Na^+]$, Table II, is not an isolated chemical artifact. Several related observations occur in the literature. Butler and Taube[16] have ascribed rate variations in $NaClO_4$ media to changes in the activities of the reacting species and of the activated complex rather than to their being a manifestation of a H_3O^+-dependent path for the Cr(II) reduction of $Co(NH_3)_5X^{n+}$ where X = glycolate and lactate. The acid dependence reported by Fraser[17] for the vanadium(II) reduction of $Co(NH_3)_4C_2O_4{}^+$ in $NaClO_4$ media was reinvestigated recently by Hwang and Haim[4] using $LiClO_4$ as the background electrolyte and revealed the absence of any H_3O^+ dependent term in the rate law. Other systems in which medium effects are significant, leading to a pseudohydrogen ion dependent path in $LiClO_4$–$HClO_4$ media include[18] $Co(C_2O_4)_3{}^{3-}$–V(II), $Co(en)(C_2O_4)_2{}^-$–V(II), and $Co(en)(C_2O_4)_2{}^-$–Fe(II).

These observations direct our attention to the nature of the oxidant molecule. In all but one case, the oxalate group was present and functioned as the bridging ligand. Similar behavior is not observed when halogens or pseudohalogens are the bridging ligands.[5] Although we cannot provide a definitive operational explanation why these complexes exhibit this particular sensitivity toward background electrolytes, the following may be considered.[19] Newton and Baker have suggested that a single term in an empirical hydrogen ion dependence may be the result of fortuitous cancellation of an actual path by a medium effect.[10]

Nonbridging Ligand Effects.—The effect of nonbridging ligands on the rate of reduction reactions has been the subject of numerous investigations[5,8,14,15,20–24] and a recent review.[25]

The term "nonbridging ligand effect" has reflected a rate change attributable to the influence of a group positioned adjacent to the ligand functioning as a bridge in an inner-sphere process for complexes having a cis

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(13) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 5343 (1966).

(14) C. Bifano and R. G. Linck, *J. Amer. Chem. Soc.*, **89**, 3945 (1967).

(15) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970).

(16) R. D. Bulter and H. Taube, *J. Amer. Chem. Soc.*, **87**, 5597 (1965).

(17) R. T. M. Fraser, *ibid.*, **85**, 1747 (1963).

(18) B. Grossman and A. Haim, *ibid.*, **93**, 6490 (1971). When this is considered as a medium effect, the charge on the complex is more important than the presence of the oxalate group.

(19) Although speculative, it may be possible that sodium ions become associated with the terminal oxygen atoms of the oxalate group, thus promoting adjacent attack by iron(II) rather than a double bridged activated complex.

(20) D. E. Pennington and A. Haim, *Inorg. Chem.*, **5**, 1887 (1966).

(21) P. R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, **91**, 3769 (1969).

(22) R. C. Patel and J. F. Endicott, *ibid.*, **90**, 6364 (1968).

(23) W. G. Movias and R. G. Linck, *ibid.*, **92**, 2677 (1970).

(24) R. G. Linck, *Inorg. Chem.*, **7**, 2394 (1968), **9**, 2529 (1970).

(25) J. E. Earley, *Progr. Inorg. Chem.*, **13**, 243 (1970).

geometry. In the discussion to follow we will treat nonbridging ligands as enities positioned trans to possible bridging groups.

The demonstrated efficiency of coordinated sulfur to function as an electron-transfer bridge[6,7] required that we examine the possibility of electron transfer occurring *via* an iron(II)–thioether bridge rather than *via* an oxalate bridge. Complexes of the type Co(eee)(1,10-phen)$^{3+}$, Co(eee)(α,α'-dipy)$^{3+}$, and Co(eee)(acac)$^{2+}$ were unreactive relative to the Co(eee)$C_2O_4^+$ reduction, not being complete over 12 hr at 25° and 0.02 *M* iron(II). This suggests reduction is not occurring *via* a sulfur bridge.[26]

A comparison of rates and available activation parameters for the iron(II) reduction of several cobalt(III) complexes is presented in Table IV.

TABLE IV

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE IRON(II) REDUCTION OF COBALT(III) COMPLEXES

Oxidant	k_t, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Co(eee)$C_2O_4^+$	1.65	10.7	−21.5
Co$(NH_3)_4C_2O_4^+$	4.16×10^{-4}	18.5	-12.1^a
Co(en)$_2C_2O_4^+$	Reaction not complete after 30 hr^b		
Co(trien)$C_2O_4^+$	Reaction not complete after 30 hr^b		
Co(en)$(C_2O_4)_2^-$	3.15×10^{-3}	15.7	-17.5^c

^{a} 25°, $\Sigma[ClO_4^-] = 1.0$ *M*.[4] ^{b} 25°, $\Sigma[ClO_4^-] = 1.0$ *M*, [Fe(II)] = 0.02 *M*, $[H_3O^+] = 0.30$ *M*, [Co(III)] = 10^{-3} *M*, $LiClO_4$–$HClO_4$ media, trien = $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$. ^{c} 25°, $[H_3O^+] = 0.6$ *M*, $LiClO_4$–$HClO_4$ media.[18]

Examination of Table IV shows that Co(eee)$C_2O_4^+$ is reduced 3.9×10^3 times more rapidly than the corresponding tetraammine analog. Also it exhibits a lower enthalpy of activation and a significantly more negative entropy of activation. The effect of replacing ammine groups by ethylenediamine and then triethylenetetramine suggests that increased chelation is not an important factor in explaining the rapidity of the Co(eee)$C_2O_4^+$–Fe^{2+} reduction. Examination of molecular models shows the absence of unusual solvation or steric interactions which might facilitate electron transfer. The net charge carried by the complex also does not appear to be as significant a rate enhancement factor as one might anticipate.

Superficially we can adopt the view that d_{z^2} orbital stabilization and the ease with which the ligand trans to the bridge can be stretched are responsible for rate enhancement. By choosing the O–Co–S axis as being coincident with the d_{z^2} orbital, the trend in reactivity parallels a decrease in field strength of the donor atom positioned trans to the bridging oxalate oxygen atom, thioether being considerably weaker than oxygen, secondary amine, primary amine, and ammonia, respectively.[3]

Although the above model provides an intuitively reasonable explanation for a qualitative rate increase, the thioether systems direct our attention to the electronic states related to the Co(III)–sulfur bond. This feature has not been investigated by many; however, Linck has attempted to develop relevant bonding criteria.[14] More recently Fleischer and Krishnamurthy[27] demonstrated a labilizing effect which has origins in the delocalized electronic structure of a ligand–metal aggregate causing cobalt(III) to loose its d^6 electronic character. The two thioether donors present in Co(eee)$C_2O_4^+$ may function in a similar way to delocalize energy states which facilitate reduction of the cobalt(III) center.

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(26) Care should be exercised with iron(II) reactions to distinguish the thermodynamic feasibility of a reaction from the rate of reaction. Co(eee)(*o*-phen)$^{3+}$ is expected to be a poorer oxidant than Co(eee)$C_2O_4^+$; however, Co(eee)(acac)$^{3+}$ should be comparable.

(27) E. B. Fleischer and M. Krishnamurthy, *J. Amer. Chem. Soc.*, **93**, 3784 (1971).