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Effect of Coordinated Sulfur in the Iron(II) Reduction of s-cis-Diazido(1,8-diamino-3,6-dithiaoctane)cobalt(III) Perchlorate

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We have been interested in the preparation, characterization, and reaction kinetics of diacidocobalt(III) complexes featuring flexible tetradentate chelating agents containing sulfur donor atoms. Much current interest has stimulated research dealing with the influence of coordinated sulfur on geometrical stereospecificity,[1] specific and dramatic trans labilization,[2] and rate retardation[3] in substitution reactions, as well as pronounced rate enhancement in electron-transfer reactions.[4]

Continuing work in our laboratory is directed toward examining the oxidation of hexaaquoiron(II) ion by various cobalt(III) complexes possessing thioether ligands positioned cis and/or trans to potential inner-sphere bridging ligands. This report presents kinetic data on the reaction between the symmetrical cis isomer of the (1,8-diamino-3,6-dithiaoctane)diazidocobalt(III) cation[5] and hexaaquoiron(II) in lithium perchlorate–perchloric acid media. These data provide the first opportunity for an overview of the s-cis-Co(NSSN)X$_2^+$ (X$^-$ = N$_3^-$, Cl$^-$; X$_2$ = C$_2$O$_4^{2-}$) family reactivities toward iron(II).[4b,c] Both Co(NSSN)Cl$_2^+$ and Co(NSSN)C$_2$O$_4^+$ react with iron(II) 10^3 times faster than their corresponding tetraammine analogues.[6] The present study shows that this enhancement is not realized in the reaction between iron(II) and s-cis-Co(NSSN)(N$_3$)$_2^+$.

Experimental Section

Materials. Stock solutions of HClO$_4$ and iron(II) perchlorate were prepared and standardized as reported earlier.[4c,6c,7] The total [ClO$_4^-$] in all solutions was determined by both gravimetric (AsPh$_4$ClO$_4$) and anion-exchange techniques. Supporting electrolytes of LiClO$_4$ and Ba(ClO$_4$)$_2$ were prepared by HClO$_4$ neutralization of Li$_2$CO$_3$ or Ba(OH)$_2$·8H$_2$O followed by standardization of anion, cation, and acid using ion-exchange and titrimetric techniques.

Kinetic Measurements. All reagents except iron(II) were placed in a thermostated cell (5.0 or 10.0 cm) in a temperature-controlled cell holder in the Cary 14. Iron(II) was delivered by syringe and the reaction monitored at 545 nm for 8–10 half-lives. In all experiments strict temperature control was maintained and pseudo-first-order conditions prevailed with respect to iron(II). Optical density–time data (D_0, D_t, D_∞, t) were treated in the usual way.[4b] Plots of ($D_t - D_\infty$) vs. time were linear for 90–95% of the reaction. All reported rate constants ($k_t = k_{obsd}/[Fe^{2+}]$) are an average of three to six individual determinations at the specified conditions. The error limits given are average deviations.

Results

General Considerations. The stereochemistry of Co(NSSN)(N$_3$)$_2^+$ allows three geometric isomers (I–III). We

I	II	III
symmetrical cis	unsymmetrical cis	trans
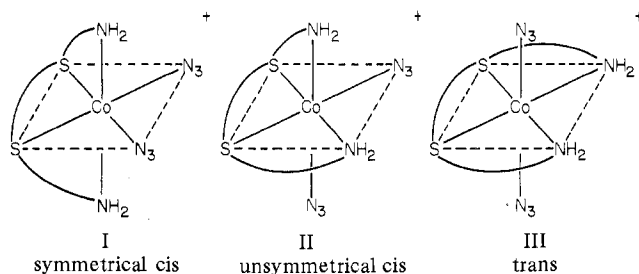
have examined several different synthetic routes to Co-(NSSN)(N$_3$)$_2^+$ by the use of interconversion reactions and, in conjunction with visible electronic and infrared spectra,

Table I. Iron, Complex, and Temperature-Dependence Data for the Reduction of s-cis-Co(NSSN)(N$_3$)$_2^+$ ^{a}

t, °C	10^4[complex], M	[Fe(II)], M	k_t, M^{-1} s^{-1}
20.8	3.1–3.3	0.031	0.094 ± 0.002
25.0	3.0–3.3	0.010	0.146 ± 0.003
25.0	2.8–3.0	0.031	0.149 ± 0.003
25.0	3.1–3.3	0.050	0.141 ± 0.005
25.0	2.8–3.1	0.070	0.143 ± 0.002
25.0	2.9–3.9	0.090	0.147 ± 0.002
30.3	3.1–3.3	0.031	0.223 ± 0.005
34.2	3.0–3.1	0.031	0.365 ± 0.002

^{a} ΣClO$_4^-$ = 1.0 M, adjusted with LiClO$_4$; [H$_3$O$^+$] = 0.40 M.

conclude that it possesses the s-cis geometry. By treating authentic s-cis-[Co(NSSN)Cl$_2$]Cl with NaN$_3$ we obtain [Co(NSSN)(N$_3$)$_2$]ClO$_4$. This latter compound can be reconverted to the original s-cis-Co(NSSN)Cl$_2^+$ by treatment with concentrated HCl. It also can be converted into other derivatives, e.g., Co(NSSN)(NO$_2$)$_2^+$, all of which have been characterized by visible, IR, ORD, and CD spectra and are known to possess the s-cis geometry.[1a]

The electronic absorption spectrum of s-cis-Co(NSSN)-(N$_3$)$_2^+$ is characterized by a single symmetrical intense envelope at 5450 Å, having a molar extinction coefficient of 722 ± 8 M^{-1} cm^{-1} and two ultraviolet absorptions at 3360 and 2200 Å (ϵ 16 000 and 15 800 M^{-1} cm^{-1}).

Acid-Catalyzed Aquation. The reduction studies reported here for Co(NSSN)(N$_3$)$_2^+$ are not complicated by aquation. Both the normal and acid-catalyzed aquations of Co-(NSSN)(N$_3$)$_2^+$, even in 1.0 M HClO$_4$, are very slow compared to reduction by 0.05 M iron(II).

Several observations concerning the aquation product Co(NSSN)(N$_3$)(H$_2$O)$^{2+}$ provide the first indication that isomerization may occur, perhaps being a route to the other geometric isomers that have thus far escaped detection and isolation. Treatment of s-cis-Co(NSSN)(N$_3$)$_2^+$ with 11.8 M HClO$_4$ results in the quantitative generation of s-cis-Co-(NSSN)(H$_2$O)$_2^{3+}$. If s-cis-Co(NSSN)(N$_3$)$_2^+$ is allowed to aquate at 25 °C in 0.8 M HClO$_4$, the spectrum slowly changes over a period of 48 h, with λ_{max} shifting from 545 to 537 nm and ϵ increasing from 722 to 837 M^{-1} cm^{-1}. If this mixture is allowed to react further, the burgundy color and the spectrum of the solution gradually fade, suggesting decomposition of the complex. Further, the burgundy complex formed by the normal aquation of s-cis-Co(NSSN)(N$_3$)$_2^+$ in 0.8 M HClO$_4$ is unchanged when treated with Hg^{2+} and/or concentrated HClO$_4$. It decomposes rather than forming the familiar s-cis-Co(NSSN)(H$_2$O)$_2^{3+}$.

Attempts to isolate the burgundy complex, believed to be [Co(NSSN)(H$_2$O)N$_3$](ClO$_4$)$_2$, failed. The reactivity of Co(NSSN)(H$_2$O)N$_3^{2+}$ toward iron(II) is especially noteworthy. Exploratory work gives a second-order rate constant of 26 M^{-1} s^{-1} for its reduction by iron(II) (25 °C, 0.8 M HClO$_4$). The linearity of the kinetic plots over 95% of the reaction strongly suggests a single cobalt(III) complex as reactant.

Reduction of s-cis-Co(NSSN)(N$_3$)$_2^+$ by Iron(II). In 1 M perchlorate (25.0 °C, 0.40 M HClO$_4$), the iron(II) reduction of s-cis-Co(NSSN)(N$_3$)$_2^+$ is first order in both reactants. Table I presents this data which is consistent with the rate law

$$-d[Co(NSSN)(N_3)_2^+]/dt = k_t[Co(NSSN)(N_3)_2^+][Fe^{2+}] \quad (1)$$

Values of k_t were determined at 20.8, 25.0, 30.3, and 34.2 °C. Activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were 17.1 kcal/mol and −5.2 eu, respectively.

Reduction Rate as a Function of Acid Concentration. Data in Table II summarize the increase in k_t from 0.132 ± 0.002

Table II. Rate Constants for the Reduction of s-cis-
Co(NSSN)(N$_3$)$_2$$^+$ by Iron(II) in Aqueous LiClO$_4$–HClO$_4$ at Constant
ClO$_4$$^-$ Concentration[a]

[H$_3$O$^+$], M	k_t, M^{-1} s^{-1}	[H$_3$O$^+$], M	k_t, M^{-1} s^{-1}
0.10	0.132 ± 0.002	0.50	0.142 ± 0.002
0.20	0.133 ± 0.002	0.60	0.145 ± 0.002
0.30	0.136 ± 0.002	0.70	0.148 ± 0.002
0.40	0.139 ± 0.001	0.80	0.151 ± 0.003

[a] Total [ClO$_4$$^-$] = 1.0 M; t = 25 °C; [Fe(II)] = 0.062 M; [complex] = 3.0 × 10^{-4} M; each k_t represents three to five individual determinations at the stated conditions; ionic strength = 1.15 M.

Table III. Acid Dependence on the Rate Constants for the Reduction of s-cis-Co(NSSN)(N$_3$)$_2$$^+$ by Iron(II) in Aqueous HClO$_4$[a]

[H$_3$O$^+$], M	total [ClO$_4$$^-$], M	k_t, M^{-1} s^{-1}
0.20	0.322	0.132 ± 0.002
0.40	0.522	0.144 ± 0.001
0.60	0.722	0.149 ± 0.003
0.80	0.922	0.160 ± 0.002
0.90	1.022	0.160 ± 0.003
1.00	1.122	0.162 ± 0.001

[a] Ionic strength was allowed to vary as a function of acid concentration. No added LiClO$_4$; t = 25.0 °C; [Fe(II)] = 0.055 M; [complex] = 3.0 × 10^{-4} M.

Table IV. Acid Dependence for the Reduction of s-cis-
Co(NSSN)(N$_3$)$_2$$^+$ by Iron(II) in Aqueous
Ba(ClO$_4$)$_2$–HClO$_4$ Media[a]

[H$_3$O$^+$], M	[Ba^{2+}], M	ionic strength	k_t, M^{-1} s^{-1}
0.15	0.365	1.428	0.139 ± 0.001
0.25	0.315	1.378	0.144 ± 0.001
0.30	0.290	1.354	0.145 ± 0.001
0.50	0.190	1.253	0.152 ± 0.001
0.70	0.090	1.155	0.155 ± 0.001
0.80	0.040	1.105	0.163 ± 0.001

[a] Total [ClO$_4$$^-$] maintained at 1.00 M with Ba(ClO$_4$)$_2$; [Fe(II)] = 0.055 M; t 25.0 °C; [complex] = 3.0 × 10^{-4} M.

M^{-1} s^{-1} at 0.10 M HClO$_4$ to 0.151 ± 0.003 M^{-1} s^{-1} at 0.80 M HClO$_4$ at μ = 1.15. Total perchlorate was maintained at 1.0 M using lithium perchlorate. The observed 14% increase in rate may be interpreted chemically as a first-order acid component or as a medium effect. In an attempt to evaluate a possible medium effect, k_t was further determined as a function of (a) [HClO$_4$], allowing total perchlorate concentration to vary, and (b) [HClO$_4$], maintaining total perchlorate concentration at 1.0 M with Ba(ClO$_4$)$_2$ instead of LiClO$_4$.

Tables III and IV summarize the results of these studies. We find that a 72% change in [ClO$_4$$^-$] from 0.322 to 1.12 M is accompanied by a 22% increase in k_t. A proportionate increase in k_t is observed also (Table II) over the 0.10–0.80 M acid range even when the total [ClO$_4$$^-$] is maintained at 1.0 M; therefore the effect of ClO$_4$$^-$ on the rate coefficient, as a medium effect, is minimal. It is observed that a 14–23% increase in k_t also occurs as a function of acid concentration whether μ is maintained at 1.15 M (Table II) or is allowed to vary from 0.36 to 1.2 M (Table III).

The acid dependence for the reduction was also examined in aqueous Ba(ClO$_4$)$_2$–HClO$_4$ solution (total [ClO$_4$$^-$] = 1.0 M) with the expectation that the large difference in activity coefficients for Li$^+$ and Ba^{2+} would invoke a major change in k_t if a significant medium effect were operative. Table IV illustrates a 17% increase in k_t from 0.139 to 0.163 M^{-1} s^{-1} as [H$_3$O$^+$] is increased from 0.15 to 0.80 M. By comparing the values of k_t in Table IV with the values in Table II, one concludes that the presence of Ba^{2+} does not result in an enhanced medium effect.

Scheme I

$$\text{Co(NSSN)(N}_3\text{)}_2{}^+ + \text{H}^+ \xrightleftharpoons{1/K_a} \text{Co(NSSN)(N}_3\text{)}_2\text{H}^{2+}$$

$$k_t{}^0 \downarrow \text{Fe}^{2+} \qquad\qquad k_\text{H} = K_a k' \downarrow \text{Fe}^{2+}$$

$$\text{Co(II)} + \text{Fe(III)} + \text{ligands} \qquad \text{Co(III)} + \text{Fe(III)} + \text{ligands}$$

Table V. Fe(II) Reduction Rates for Azido Cobalt(III) Complexes[6b]

complex	k_t, M^{-1} s^{-1}
Co(NH$_3$)$_5$N$_3$$^{2+}$	0.0087
trans-Co(en)$_2$ClN$_3$$^+$	0.062[a]
trans-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$	0.073
cis-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$	0.185
cis-Co(NSSN)(N$_3$)$_2$$^+$	0.145
cis-Co(NH$_3$)$_4$(H$_2$O)N$_3$$^{2+}$	0.355
trans-Co(NH$_3$)$_4$(N$_3$H)N$_3$$^{2+}$	>1.37
trans-Co(NH$_3$)$_4$(H$_2$O)N$_3$$^{2+}$	24
Co(NSSN)(H$_2$O)N$_3$$^{2+}$	26
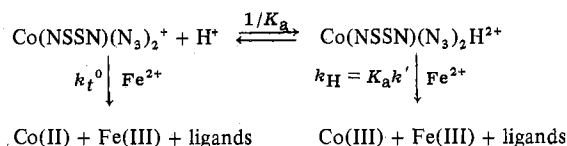
[a] Reference 6c, t = 25 °C, Σ[ClO$_4$$^-$] = 1.0 M.

The dependence of k_t on [H$_3$O$^+$] at 25 °C for either LiClO$_4$ or Ba(ClO$_4$)$_2$ as supporting electrolyte is adequately represented by the equation

$$k_t = k_t{}^0 + k^\text{H}[\text{H}_3\text{O}^+] \tag{2}$$

Graphically, we calculate $k_t{}^0$ to be 0.127 ± 0.002 M^{-1} s^{-1} and k^H as 0.030 ± 0.001 M^{-2} s^{-1} for the LiClO$_4$ case. The corresponding values for $k_t{}^0$ and k^H in aqueous Ba(ClO$_4$)$_2$–HClO$_4$ media are 0.134 ± 0.002 M^{-1} s^{-1} and 0.032 ± 0.001 M^{-2} s^{-1}.

Discussion

Medium Effect Considerations. When an apparent [H$^+$]-dependent term is observed and the overall variation in k_t is small (~10–24%), there is the possibility that a medium effect is operative.[8–16] Often a test for this effect employs equations[17] simplified by Newton and others[8–16] and rate data obtained at high acidities (2–4 M) and constant ionic strength (~4 M).[14,15] Like many azide complexes, Co(NSSN)(N$_3$)$_2$$^+$ is not amenable to studies at high acidities (>1.5 M) without the introduction of competitive reactions. The trends in k_t in both LiClO$_4$ and Ba(ClO$_4$)$_2$ media are consistent yet small and may be interpreted as a medium effect[17] or as a two-path reduction with the dominant path in the Co(NSSN)-(N$_3$)$_2$$^+$–Fe^{2+} reaction being acid independent and the minor path being acid dependent; see Scheme I. We favor the latter interpretation.

Fe(II) Reduction of Other Azide Complexes. Table V summarizes the iron(II) reduction rates for several cobalt(III) complexes which are structurally similar to s-cis-Co-(NSSN)(N$_3$)$_2$$^+$. The particular reactivity trends in k_t have been attributed by Haim and co-workers[6] to the circumstance that the d$_{z^2}$ orbital that accepts the electron is made available by simultaneously removing the bridging ligand and the group trans to it.[18]

In terms of reactivity, s-cis-Co(NSSN)(N$_3$)$_2$$^+$ is very similar to cis-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$. Surprisingly, the natural aquation product, presumed to be Co(NSSN)(H$_2$O)N$_3$$^{2+}$, has a reactivity almost identical with that of trans-Co(NH$_3$)$_4$-(H$_2$O)N$_3$$^{2+}$. This observation suggests a trans geometry for Co(NSSN)(H$_2$O)N$_3$$^{2+}$. The fact that it decomposes after aquation is not inconsistent with the trans structure based on earlier observations concerning the aquation of Co-(NSSN)Cl$_2$$^+$.[3,19]

A comparison of reactivities for the NSSN series[4b,c,20] Co(NSSN)Cl$_2$$^+$, Co(NSSN)Br$_2$$^+$, Co(NSSN)C$_2O_4$$^+$, and Co(NSSN)(N$_3$)$_2$$^+$ allows us to compare the relative efficiency of the bridging ligands, assuming an inner-sphere mechanism.

Table VI. Thermodynamic Parameters for the Reduction of $Co(NSSN)X_2^{n+}$ Complexes[a]

complex	$k_t, M^{-1} s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol
$Co(NSSN)Cl_2^+$	1.66	10.5	−22.4	17.2
$Co(NSSN)C_2O_4^+$	1.65	11.3	−19.8	17.2
$Co(NSSN)(N_3)_2^+$	0.145	17.1	−5.2	18.6
$Co(NSSN)Br_2^+$	0.097	12.1	−22.9	18.9

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

The iron(II) reduction rates for $Co(NH_3)_4XY^{n+}$ and $Co(en)_2XY^{n+}$ type complexes follow a general rate pattern $N_3^- \gg Cl^- > Br^- > C_2O_4^{2-}$, whereas in this series we find $Co(NSSN)Cl_2^+$ (1.66) $\sim Co(NSSN)C_2O_4^+$ (1.65) $\gg Co(NSSN)(N_3)_2^+$ (0.145) $> Co(NSSN)Br_2^+$ (0.085), where k_t, in $M^{-1}\ s^{-1}$, is given in parentheses. The most interesting facet is the nonreactivity of the diazido complex. Each of the other NSSN complexes is reduced by iron(II) at rates from 10^2 to 10^4 times more rapid than those of the most closely related tetraammine and/or bis(ethylenediamine) complex. A similar rate enhancement would be expected for $Co(NSSN)(N_3)_2^+$. Note also the anomalous $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the diazido complex (Table VI). These observations, in conjunction with the minor acid dependence (medium effect), point to a system which is particularly sensitive to solvent participation, ion-pairing, or bond-cleavage effects.

Registry No. s-cis-$Co(NSSN)(N_3)_2^+$, 46751-04-6; s-cis-Co-$(NSSN)Cl_2^+$, 32594-33-5; s-cis-$Co(NSSN)C_2O_4^+$, 38586-91-3; s-cis-$Co(NSSN)Br_2^+$, 46135-49-3; Fe^{2+}, 15438-31-0.

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(17) $\ln k_t = \ln k^H - n\alpha[M^{n+}]$, where k^H corresponds to the value of k_t in pure $HClO_4$, n is the cation charge of the supporting electrolyte, and α is a constant having a value presumably <0.1 for $LiClO_4$–$HClO_4$ systems obeying Harned's rule.[8a] For comparative information, the data in Tables II and IV give the following. $LiClO_4$: $\alpha = 0.198 \pm 0.01\ M^{-1}$ and $k^H = 0.152 \pm 0.001\ M^{-1}\ s^{-1}$. $Ba(ClO_4)_2$: $\alpha = 0.212 \pm 0.02\ M^{-1}$ and $k^H = 0.164 \pm 0.002\ M^{-1}\ s^{-1}$.
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## Selective Crown Ether Assistance in Ligand-Exchange Reactions of Transition-Metal Complexes

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Cation complexation by crown ethers (macrocyclic polyethers) has been an area of intense interest for the last decade.[2a] Complexation studies for a wide variety of inorganic and organic cations have appeared.[2,3] Less familiar is the association of crown ethers with neutral, but polar, molecules.[3,4] One of the best examples of such association is the formation of an acetonitrile–crown ether adduct or "complex" of variable stoichiometry[5] which is utilized in the purification of 18-crown-6, **1**. It seemed reasonable that a similar crown

1   **2**
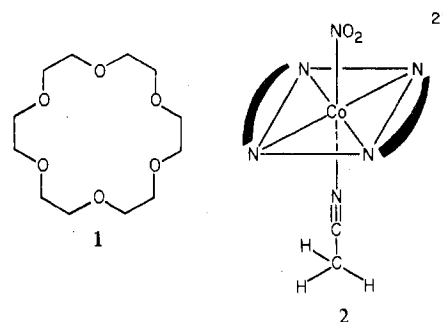
ether–acetonitrile association might enhance the exchange reactions of acetonitrile ligands from transition-metal complexes. We now report the first example of such crown assisted ligand exchange.

Clarkson and Basolo[6] previously observed changes in the ^1H NMR spectrum of *trans*-nitrobis(ethylenediamine)-acetonitrilocobalt(III) perchlorate, $[Co(en)_2(CH_3CN)-NO_2][ClO_4]_2$, **2**, when the solid was dissolved in D_2O (buffered at pD 4.4) and allowed to stand in the spectrometer probe at ambient temperature. The ^1H NMR spectrum of **2** initially exhibited a methyl resonance positioned at 2.1 ppm upfield from the HOD resonance. After the solution was allowed to stand, this methyl resonance slowly decreased in intensity and a new, permanent, single-line resonance located 2.6 ppm upfield from HOD simultaneously emerged. The ^1H NMR resonance of added excess acetonitrile superimposed perfectly upon that of the reaction product. Thus, the ^1H NMR spectral changes indicated a slow aquation of **2**, the bound acetonitrile being replaced by solvent (eq 1). Additional support for this

$$\text{2} \xrightarrow[\text{pD 4.4}]{D_2O} \text{3} + CH_3CN \qquad (1)$$
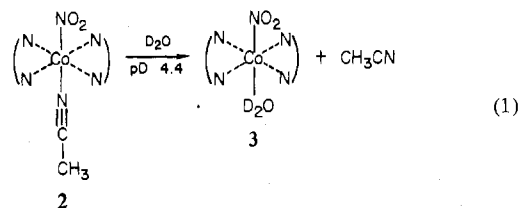
interpretation was provided by the ultraviolet–visible absorption spectrum of the reaction product which was identical with that of **3** prepared by an alternative procedure. Therefore, ^1H NMR spectra appeared to be an ideal method for measuring the kinetics of acetonitrile removal from the cobalt ion coordination sphere of **2** and assessing the effect, if any, of crown