a low BDE of 15 kcal. Further discussion of the Co–Co BDE value must await a complete analysis of the variable-temperature NMR spectrum of the $Co_2(CO)_8/Mn_2(CO)_{10}/H_2$ system, as well as that for similar mixed-metal systems with stable metal-centered radicals, whose thermodynamics are unequivocally established. A prime candidate in this regard is the $[Cp^*Cr(CO)_3]_2/HCr(CO)_3Cp^*$ ($Cp^* = \eta\text{-}C_5Me_5$) system,[27] because the $Cp^*Cr(CO)_3^{\bullet}$ radical exhibits reversible electrochemistry[18] and is sufficiently stable that the enthalpy of hydrogenation of the radical has been directly measured by calorimetry.[28]

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(28) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D. *J. Am. Chem. Soc.* **1990**, *112*, 5657–5658.

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Electron-Transfer Reactions of Cobalt(III) Complexes Possessing Oxysulfur Ligands

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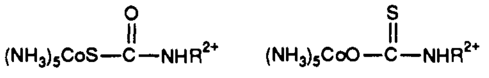
The kinetics of the chromium(II) reduction of a series of cobalt(III) complexes possessing an oxysulfur bridging ligand have been measured. At 25 °C, $I = 1.0$ M ($LiClO_4$) the second order rate constants for the pentaamminecobalt(III) complexes of SO_3^{2-}, $C_6H_5SO_2^-$, and $S_2O_5^{2-}$ are 4.7 (±0.3) × 10^3, 5.3 (±0.1) × 10^3, and 2.1 (±0.1) × 10^4 M^{-1} s^{-1}, respectively. The reduction of *trans*-$(NH_3)_4Co(OH_2)SO_3^+$ by chromium(II) has also been studied and yields a rate constant of 1.1 (±0.1) × 10^5 M^{-1} s^{-1} at 25 °C, $I = 1.0$ M ($LiClO_4$). The value of 18.6 M^{-1} s^{-1} for the rate constant for chromium(II) reduction of the sulfite complex reported in 1965 is now seen to be incorrect. The data are discussed in terms of a ground-state trans effect induced by the coordinated sulfur atom.

Introduction

A recent study of the reduction of the linkage isomers of the monothiocarbamato complexes



$(NH_3)_5CoS{-}\overset{O}{\overset{\|}{C}}{-}NHR^{2+}$ $\quad$ $(NH_3)_5CoO{-}\overset{S}{\overset{\|}{C}}{-}NHR^{2+}$

$R = CH_3, CH_2C_6H_5, C_6H_5, 4\text{-}CNC_6H_4$

by chromium(II) has shown that the unusually rapid reduction of the S-bonded complexes is mainly due to a ground-state structural trans effect (STE) in the oxidant.[1] The S-bonded sulfito complex $(NH_3)_5CoSO_3^+$ has one of the largest known STEs (0.089 Å)[2] and its rate of reduction by chromium(II) has been reported as 18.6 M^{-1} s^{-1} (25 °C).[3] This value is approximately 4 orders of magnitude less than that predicted on the basis of the STE.[4] The sulfito complex can only be prepared and purified in solutions containing free ammonia,[5] and it reacts rapidly in acidic medium to form *trans*-$(NH_3)_4Co(OH_2)SO_3^+$. The latter complex also undergoes internal redox decomposition.[6] Due to these complications and our recent findings, we have reinvestigated the reaction of $(NH_3)_5CoSO_3^+$ with Cr^{2+}. We also report kinetic data for the reduction of $(NH_3)_5CoS_2O_5^+$, $(NH_3)_5CoSO_2C_6H_5^{2+}$, and *trans*-$(NH_3)_4Co(OH_2)(SO_3)^+$ by Cr^{2+}.

Experimental Section

Materials. $[Co(NH_3)_5SO_3]ClO_4$,[7] $[Co(NH_3)_5S_2O_5]ClO_4$,[8] and $[Co(NH_3)_5(\text{benzenesulfinato})](ClO_4)_2$[2] were prepared according to literature methods. *trans*-$(NH_3)_4Co(OH_2)SO_3^+$ was prepared by dissolving $Co(NH_3)_5SO_3^+$ in water. Chromium(II) solutions were obtained via reduction of stock chromium(III) perchlorate using zinc amalgam. Concentrations were standardized as previously described.[1]

Kinetics. Reaction rates were measured using a Durrum D110 stopped-flow spectrophotometer interfaced with a computerized data acquisition system. Rate constants were obtained from processing of the raw data utilizing programs developed by the OLIS Corp. (Jefferson, GA). All rate constants are averages of three runs and are precise to at least 10%.

Ionic strength was maintained using lithium perchlorate and perchloric acid stock solution. These solutions were standardized as described previously.[1] Due to the oxygen sensitivity of chromium(II), all reactions were carried out under a blanket of argon using standard syringe techniques.

Results and Discussion

When $[(NH_3)_5CoSO_3](ClO_4)$ is dissolved in neutral or acidic solution, the visible absorption spectrum gives a maximum at 472 nm ($\epsilon = 160$ M^{-1} cm^{-1}). The latter peak indicates the presence of *trans*-$(NH_3)_4Co(OH_2)SO_3^+$ formed by the rapid substitution of the ammonia trans to the sulfito group.[6] The sulfitopentaamminecobalt(III) cation, however, persists in 0.10 M NH_3(aq) and gives a visible maximum at 456 nm ($\epsilon = 150$ M^{-1} cm^{-1}). If a solution of the sulfito complex in 0.10 M NH_3(aq) is mixed with 1.0 M $HClO_4$(aq) on a stopped-flow instrument, the formation of the trans-substituted complex is complete in approximately 2 min. The reaction can be conveniently observed at 472 nm where the expected increase in absorbance is significant. In the reduction studies all the acid was contained in the chromium(II) solutions which were then mixed with $(NH_3)_5CoSO_3^+$ in 0.10 M NH_3(aq). At 450–472 nm only an absorbance decrease was observed consistent with reduction of cobalt(III) to cobalt(II). More importantly, under these conditions, reduction of the sulfito complex was much faster (approximately 3 orders of magnitude) than the substitution reaction as observed above. The observed rate constants collected in this manner were first order in both complex

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(1) Balahura, R. J.; Johnson, M. D.; Black, T. *Inorg. Chem.* **1989**, *28*, 3933.
(2) Elder, R. C.; Heeg, M.; Payne, M.; Trkula, M.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 431.
(3) Peters, D. E.; Fraser, R. T. M. *J. Am. Chem. Soc.* **1965**, *87*, 2758.
(4) Deutsch, E.; Root, M.; Nosco, D. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 269.
(5) Siebert, H.; Wittke, G. *Z. Anorg. Allg. Chem.* **1973**, *399*, 43.
(6) Thacker, M.; Scott, K.; Simpson, M.; Murray, R.; Higginson, W. *J. Chem. Soc., Dalton Trans.* **1974**, 647.
(7) Elder, R. C.; Trkula, M. *J. Am. Chem. Soc.* **1974**, *96*, 2635.
(8) Balahura, R. J.; Johnson, M. D. *Inorg. Chem.* **1988**, *27*, 3104.

Table I. Chromium(II) Reduction Rates of Cobalt(III) Complexes Containing a Coordinated Sulfur[a]

complex	$[H^+]$, M	$[Cr^{2+}]$, M × 10^3	k_{obs}, s^{-1} [b]
$(NH_3)_5CoSO_3^+$ [c]	0.50	1.5	6.89
	0.50	3.0	15.9
	0.50	4.5	21.0
	0.50	7.5	33.1
trans-$(NH_3)_4Co(OH_2)SO_3^+$	0.50	1.2	125
	0.10	2.5	280
	0.10	1.2	130
	0.10	0.63	71
	0.20	2.5	276
$(NH_3)_5CoS_2O_5^+$	0.10	10.0	212
	0.10	5.0	106
	0.10	2.5	52.0
	0.10	1.0	21.1
	0.20	5.0	110
	0.20	1.0	22.0
	0.20	2.5	50.1
$(NH_3)_5CoSO_2C_6H_5^{2+}$	0.10	10.0	53.4
	0.10	5.0	26.1
	0.10	2.5	13.0
	0.10	1.0	5.25
	0.50	5.0	25.0
	0.50	1.0	5.80

[a] I = 1.0 M ($LiClO_4$), T = 25.0 °C, and [Co(III)] ~ 1 × 10^{-4} M. k_{obs} values are the average of at least three separate determinations and are good to 10%. [b] Rates monitored at the visible peak maximum. [c] Determined as described in the text. Shown to be qualitatively independent of $[H^+]$.

and reductant and independent of the hydrogen ion concentration. The data are given in Table I.

The metabisulfite complex $(NH_3)_5CoS_2O_5^+$ and the benzenesulfinate complex $(NH_3)_5CoSO_2C_6H_5^{2+}$ are much less labile than the sulfito species and were simply dissolved in water and used immediately (within 5 min). The reduction reactions were first order in complex and chromium(II) and were independent of $[H^+]$. These data are also given in Table I.

Kinetic data for reduction of *trans*-$(NH_3)_4Co(OH_2)SO_3^+$ by chromium(II) were obtained by generating the trans complex in situ by dissolving $(NH_3)_5CoSO_3^+$ in water. These solutions were used between 5 and 10 min after preparation. Observed rate constants were first order in complex and chromium(II) and independent of $[H^+]$. The data are given in Table I.

Due to complicating redox, isomerization, and substitution reactions of the initial chromium(III) products, isolation by cation exchange chromatography was not possible. However, in all cases, the initial chromium(III) visible spectrum was not that of $Cr(OH_2)_6^{3+}$, indicating that ligand transfer had taken place. Thus all reactions appear to follow the inner-sphere mechanism.

The complexes investigated herein have all been shown to contain a cobalt–sulfur bond by X-ray analysis[2,7] and electronic absorption and magnetic resonance spectroscopy.[2] Furthermore, the synthetic route demands sulfur-bonding in the case of the metabisulfite[8] and *trans*-aqua–sulfito[6] complexes. Thus with the exception of the thiosulfato complex, the structures almost certainly dictate attack of chromium(II) at an oxygen atom bonded to the coordinated sulfur. For the thiosulfato system, attack at oxygen is also favored, but in this case an extra sulfur is involved in the electron transfer pathway.[9]

Table II. Rate Constants and STE Data for Cobalt(III) Complexes

complex	k, M^{-1} s^{-1}	STE, Å
$(NH_3)_5CoSO_3^+$	4.7 (±0.3) × 10^3	0.089[a]
$(NH_3)_5CoSO_2C_6H_5^{2+}$	5.3 (±0.1) × 10^3	0.054[a]
$(NH_3)_5CoSSO_3^+$	8.5 × 10^2	0.026[b]
$(NH_3)_5CoSO_2SO_3^+$	2.1 (±0.1) × 10^4	*c*
trans-$(NH_3)_4Co(OH_2)SO_3^+$	1.1 (±0.1) × 10^5	*c*

[a] Reference 2. [b] Reference 9. [c] Not available.

Table II contains the rate constants obtained here as well as values for similar complexes. Also given are values for the structural trans effect where the appropriate crystallographic data are available. The rate constant obtained in this study for the reduction of $(NH_3)_5CoSO_3^+$ does not agree with the reported[3] value of 18.6 M^{-1} s^{-1}. We cannot offer any explanation for this discrepancy other than the difficulties caused by the lability of the complex and the redox activity of the rapidly formed *trans*-aqua–sulfito complex. The latter complex decomposes to $Co^{2+}(aq)$ in acidic solution with a first-order rate constant of 1.14 × 10^{-4} s^{-1} at 25 °C.[6] The value for the chromium(II) reduction of $(NH_3)_5CoSO_3^+$ obtained here, 4.7 × 10^3 M^{-1} s^{-1}, is internally consistent with the other data reported in Table II (vide infra), and our value is assumed to be the correct one.

The facility of the reduction of complexes containing a sulfur atom coordinated to cobalt(III) has been attributed to the ground-state trans effect exerted by the sulfur atom. It is argued that the weaker trans bond requires less activation in reaching the transition state. On this basis it is expected that *trans*-$(NH_3)_4Co(OH_2)SO_3^+$ would be reduced more rapidly than $(NH_3)_5CoSO_3^+$ since it is easier to stretch the Co–O bond then the Co–N bond. The values for the chromium(II) reduction of 1.1 × 10^5 and 4.7 × 10^3 M^{-1} s^{-1}, respectively, are consistent with this idea. Furthermore, based on this hypothesis, a direct correlation between the trans bond lengthening (STE) and electron transfer rate is expected. Such a relationship for SO_3^{2-}, $C_6H_5SO_2^-$ and $S_2O_3^{2-}$ has been observed for substitution of the trans NH_3 by SCN^-. However, for the chromium(II) reductions a plot of log k_{et} versus STE does not appear to be linear even though the data are in qualitative agreement with the prediction. Difficulties with the quantitative aspects of the model are not uncommon and have been discussed previously.[4] Further speculation regarding a possible quantitative relation between log k_{et} and STE is not warranted until more data become available.

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Registry No. Cr^{2+}, 22541-79-3; $(NH_3)_5CoSO_3^+$, 53108-45-5; *trans*-$(NH_3)_4Co(OH_2)SO_3^+$, 48052-50-2; $(NH_3)_5CoS_2O_5^+$, 138666-74-7; $(NH_3)_5CoSO_2C_6H_5^{2+}$, 64715-09-9.

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(9) Restivo, R.; Ferguson, G.; Balahura, R. *Inorg. Chem.* **1977**, *16*, 167.

(10) Cooper, J.; McCoy, J.; Katz, M.; Deutsch, E. *Inorg. Chem.* **1980**, *19*, 2265.