2136 *Inorg. Chem.* **1996,** *35,* 2136−2139

Electron Transfer. 128. Rate Enhancements by Donor Sulfur in Hexadentate Ligands[1]

Swapan K. Chandra* and Edwin S. Gould*

Department of Chemistry, Kent State University, Kent, Ohio 44242

Received July 13, 1995[⊗]

The cobalt(III) complexes of the hexadentate $N_2S_2O_2$-coordinating ligand, 1,8-*N*-disalicylidene-3,6-dithiaoctane-1,8-diamine (**III**) and its 3,6-diaza N_4O_2-coordinating analog (**IV**) adopt structures of type **VI**, in which O−N−S or O−N−N sequences span meridional positions. In this comparison of the rates of reduction of the two complexes (to Co^{2+} in 0.1 M H^+) using as reductants Cr(II), Eu(II), V(II), Ti(III), $Ru(NH_3)_6{}^{2+}$, and the dihydro derivative of the *N*-methylphenazinium cation, a greatly enhanced reactivity (10^3-10^6) of the $N_2S_2O_2$-bound oxidant is found to persist for both inner- and outer-sphere reductions and extends to the metal-free reductant as well. It is suggested that the higher rates for the S_2-bound system reflect the acquisition of a quasiaromatic character in the $(S)_2Co^{III}$ arm of this oxidant, within which electron transfer to the metal center requires less severe stretching of the metal-ligand bonds than is necessary for N- and O-ligated complexes. The augmentation in $k_{Cr(II)}$ values of carboxylato complexes of Co(III) on incorporation of α-thio substituents may, on the other hand, stem from an increased degree of conversion to a chelated Co(III)−Cr(II) precursor, **VII**, which is stabilized partially by back-bonding involving interaction of the e_g electron of Cr(II) and a d-orbital of sulfur. In contrast to the reactions of oxidants featuring donor sulfur in the primary coordination sphere, this mode of acceleration does not extend to reductions by V^{2+}, Eu^{2+} or Ti(III) (which are devoid of e_g electrons) or to the outer-sphere reductions by $Ru(NH_3)_6{}^{2+}$. It is, however, observed with the d^{10} reductant, Cu^+.

The realization that thio and mercapto groups may facilitate electron transfer acts involving metal centers is based, in large part, on results generated in two quite different lines of endeavor. For workers dealing with biosystems, the importance of the ferredoxins and high potential iron−sulfur proteins as cofactors in a variety of redox processes[2] cannot be overemphasized, and it has been recognized since the mid-1960s that these species are characterized by sulfur-bridged Fe−S clusters.[3] At nearly the same time, experiments with *in vitro* inorganic systems likewise yielded evidence of redox acceleration resulting from incorporation of donor sulfur functions.

An early hint in this direction[4] was the reported 15-fold enhancement in the specific rate (k_{Cr}) of Co(III) reduction, using Cr^{2+}, when an *S*-benzyl group was attached to the acetato ligand in $Co(NH_3)_5(OAc)^{2+}$ (**II**):

$$CH_3CO_2Co(NH_3)_5{}^{2+} \qquad C_6H_5CH_2SCH_2CO_2Co(NH_3)_5{}^{2+}$$

$$\mathbf{I};\ k_{Cr} = 0.35 \qquad \mathbf{II};\ k_{Cr} = 5.2$$

The increase is a modest one, for the sulfur is not bound directly to the Co(III) center, nor can it function as a "lead-in" site. Moreover, the effect was subsequently overshadowed by much more striking accelerations reported by Bennett,[5] Haim,[6] and Balahura[7] (see Table 1).[8] Analogous enhancements in rates of reduction by Fe^{2+} have been described by Worrell.[9] Moreover, Rorabacher and co-workers[10] have estimated a rate constant of $10^{3.8\pm0.2}$ M^{-1} s^{-1} for Cu(I,II) self-exchange in S_4-ligated copper centers, a value about 10^{13} times the upper limit (10^{-9} M^{-1} s^{-1})[11] taken to apply to aqua-substituted systems.

Table 1. Rapid Reductions of S-Ligated Cobalt(III)

oxidant	k_{Cr}, M^{-1} s^{-1} [a]	site of attack	ref
$[(en)_2Co^{III}S(CH_3)CH_2COO]^{2+}$	274	=O	5b
$[(en)_2Co^{III}SCH_2CH_2NH_2]^{2+}$	3.3×10^4	−S−	5c
$[(en)_2Co^{III}SCH_2COO]^{+}$	6.4×10^6	=O	5c
$[(NH_3)_5Co^{III}SC(=O)NHCH_3]^{2+}$	6.4×10^4	=O	7
$[(NH_3)_5Co^{III}SCN]^{2+}$	1.9×10^6	≡N[b]	6
	8×10^5	−S−[b]	

[a] Reductions by Cr^{2+}(aq); 25 °C, $\mu = 1.0$ M. [b] Competing sites.

This type of acceleration has been attributed, at least in part, to a structural trans effect,[8] an elongation of the metal−ligand bond lying trans to the donor sulfur, which is presumed to stabilize the acceptor orbital of the oxidant and hence lower the activation energy and increase the rate associated with electron transfer. Crystal structure determinations of a number of Co(III)−S complexes have confirmed such a bond extension in some[8,12] but not all[13] instances.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

(1) Sponsorship of this work by the National Science Foundation (Grant 9414113) is gratefully acknowledged.

(2) See, for example: (a) Mortenson, L. E.; Nakos, G. In *Iron-Sulfur Proteins*; Lovenberg, G., Ed.; Academic Press: New York, 1973; Vol. 1, Chapter 2. (b) Hay, R. W. *Bio-Inorganic Chemistry*; Ellis Horwood Ltd.: Chichester, England, 1987; pp 165−176. (c) Holm, R. H.; Ciurli, S.; Weigel, J. A. *Prog. Inorg. Chem.* **1990**, *38*, 1−74. (d) Tanaka, K.; Tanaka, T. *Inorg. Chem.* **1984**, *23*, 518.

(3) See, for example: (a) Gibson, J. F.; Hall, D. O.; Thornley, J. H. M.; Whatley, F. R. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *56*, 987. (b) Brintzinger, H.; Palmer, G.; Sands, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *55*, 397. (c) Sieker, L. C.; Adman, E.; Jensen, L. H. *Nature (London)* **1972**, *235*, 40.

(4) Gould, E. S. *J. Am. Chem. Soc.* **1965**, *87*, 4730. Rate constants (M^{-1} s^{-1}) pertain to reactions at 25 °C; $\mu = 1.5$ M.

(5) (a) Lane, R. H.; Bennett, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 1089. (b) Gilroy, M.; Sedor, F. A.; Bennett, L. E. *J. Chem. Soc., Chem. Commun.* **1972**, 181. (c) Lane, R. H.; Sedor, F. A.; Gilroy, M. J.; Eisenhardt, P.; Bennett, J. P., Jr.; Ewall, R. X.; Bennett, L. E. *Inorg. Chem.* **1977**, *16*, 93.

(6) Shea, C.; Haim, A. *J. Am. Chem. Soc.* **1971**, *93*, 3055.

(7) Balahura, R. J.; Johnson, M.; Black, T.; *Inorg. Chem.* **1989**, *28*, 3933.

(8) Similar acceleration has been mentioned: Elder, R. C.; Florian, L. R.; Lake, R. E.; Yacynych, A. M. *Inorg. Chem.* **1973**, *12*, 2690.

(9) (a) Worrell, J. H.; Jackman, T. A. *J. Am. Chem. Soc.* **1971**, *93*, 1045. (b) Worrell, J. H.; Goddard, R. A.; Gupton, E. M.; Jackman, T. A. *Inorg. Chem.* **1972**, *11*, 2734.

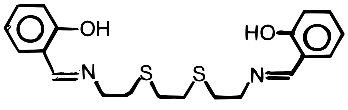
(10) Meagher, N. E.; Juntunen, K. L.; Salhi, C. A.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 10411.

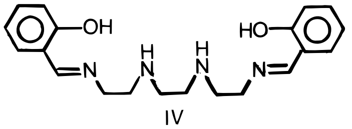
(11) See, for example: Pillai, G. C.; Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 1868.

0020-1669/96/1335-2136$12.00/0

To the extent that such rate enhancements can be linked to ground state structural features of the oxidant, we should anticipate that these accelerations will occur with a variety of reducing agents. In the few cases where such Co(III)−S oxidants have been treated with reductants other than Cr(II),[5c,9,14] this appears to be so.

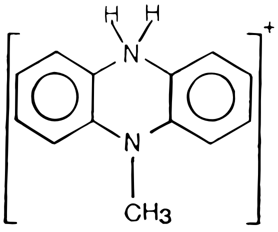
The ease with which the linear hexadentate ligands 1,8-*N*-disalicylidene-3,6-dithiaoctane-1,8-diamine (**III**) and its 3,6-diaza analog (**IV**) can be prepared and converted to their cobalt(III) derivatives[15] have prompted us to examine the redox chemistry of these complexes and thus to compare the effects of S- and N-ligation in two otherwise very similar oxidants. Included in the group of metal-center reductants employed are Eu(II) and Ti(III). Reactions of the latter two states with S-bound Co(III) appear to have been overlooked.


III


IV

Experimental Section

Materials. Lithium perchlorate[16] (for kinetic experiments) and aqueous solutions of the salts $Eu(ClO_4)_2$,[17] $V(ClO_4)_2$,[18] $Cr(ClO_4)_2$,[19] $Ru(NH_3)_6Cl_2$,[20] $TiCl_3$,[21] and $CuClO_4$[22] were prepared by literature methods. Solutions of the dihydro derivative of the *N*-methylphenazinium ion (**V**) were prepared by V^{2+} reduction of the methosulfate salt of the parent aromatic *N*-methylphenazinum cation (Aldrich) as described by Singh and co-workers.[23]


V

The green cobalt(III) complex of the $N_2S_2O_2$-coordinating ligand **III**[15c] and the dark brown complex of the N_4O_2 ligand **IV**[15b] were synthesized by literature procedures. The chloride salt of the latter was converted to the corresponding perchlorate salt by passage through anion exchange resin (Amberlite CG-400, 100−200 mesh, ClO_4^- form. The crystalline perchlorate was then precipitated by addition of saturated $NaClO_4$, filtered off, and dried over P_2O_5. UV−vis for **III** (CH_3CN): λ_{max} 680 ($\epsilon = 675\ M^{-1}\ cm^{-1}$), 460 nm ($\epsilon = 967$); lit.[15c] 680 ($\epsilon = 670$), 460 ($\epsilon = 970$). UV−vis for **IV** ($CH_3OH$): λ_{max} 590 ($\epsilon = 153\ M^{-1}\ cm^{-1}$); 388 nm ($\epsilon = 5.21 \times 10^3$); lit.[15b] 590 ($\epsilon = 155$), 388 ($\epsilon = 5.20 \times 10^3$).

Table 2. Stoichiometries of Reductions of Cobalt(III) Derivatives of Hexadentate Ligands[a]

oxidant	reductant	$[Co^{III}]$, mM	[red], mM	yield of Co(II)[b]
$[Co^{III}(N_2S_2O_2{}^{2-})]^{+}$ [c]	Cr^{2+}	2.7	1.40	1.00
		2.4	0.98	0.97
	V^{2+}	2.7	1.40	0.98
		2.4	0.98	0.96
	Eu^{2+}	0.92	0.46	0.93
	$Ru(NH_3)_6{}^{2+}$	1.80	0.96	0.99
		1.80	0.60	0.95
$[Co^{III}(N_4O_2{}^{2-})]^{+}$	Cr^{2+}	8.0	3.9	0.92
		8.8	1.90	0.94

[a] Reductions of the Co(III) complexes of the dianions of ligands **III** and **IV** were carried out at 25 °C in 0.10 M $HClO_4$. Waiting period 10 min. [b] $[Co^{II}]_{formed}/[red]_{added}$. $[Co^{II}]$ was measured at 692 nm.[19] [c] Reactions in 98/2 H_2O-CH_3CN.

Stoichiometry Experiments. Stoichiometric determinations,[19] in which cobalt(III) and the ligand bound to it were allowed to compete for added reducing agent, were carried out by adding a known deficiency of the reductant to a measured quantity of the Co(III) oxidant in 0.1 M $HClO_4$ under N_2. After a 10 min waiting period, the resulting Co(II) was estimated as $CoCl_4{}^{2-}$ as described.[19] Results are summarized in Table 2. In addition, it was shown that the unbound $N_2S_2O_2$ ligand (**III**, 0.010 M) was not perceptibly reduced (within 10 min) by any of the four reductants (0.005−0.007 M) used in this study, nor was the N_4O_2 ligand (**IV**) reduced with Cr^{2+} under similar conditions.

Kinetic Studies. Reactions of Cr(II), V(II), Eu(II), Ti(III), and *N*-methyldihydrophenazinium cation were carried out under N_2, and those of $Ru(NH_3)_6{}^{2+}$ were run under argon. Conversions were monitored using a Beckman Model 5260 or Cary 14 recording spectrophotometer or a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Reductions of the Co(III)−$N_2S_2O_2$ complex were followed at 665 nm, whereas those of the Co(III)−N_4O_2 oxidant were observed at 584 nm. Ionic strength, which was maintained at 0.10 M for most reactions, was regulated by addition of $LiClO_4$ and $HClO_4$ or, in the case of reductions by $Ru(NH_3)_6{}^{2+}$, by addition of HCl. Because the $N_2S_2O_2$ complex dissolves with difficulty in water, solutions of this oxidant were prepared by dissolving the solid compound in a small volume of CH_3CN, then diluting 50-fold with the aqueous supporting medium.[24] Excess quantities of the reductant were used in all kinetic runs, and concentrations were generally adjusted so that no more than 10% of the latter was consumed. All reactions yielded simple exponential curves; rate constants were obtained by nonlinear least squares fitting to the relationship describing first order decay. Values calculated from replicate runs agreed to better than 4%. All reactions were first order in both redox partners. Specific rates greater than 50 s^{-1} were adjusted upward to accommodate the mixing rate associated with the stopped-flow instrument, as described by Dickson.[25] Possible rate variations with changes on acidity were examined for reductions with Cr(II), Eu(II), and Ti(III), but not for reductions with V(II) and $Ru(NH_3)_6{}^{2+}$; such variation is much less usual with the latter two reductants.[17b,20,26] Reactions of both oxidants with Cu^+ were immeasurably slow; only upper limits could be obtained for this reductant.

---

(12) (a) Palmer, J. M.; Deutsch, E.; *Inorg. Chem.* **1975**, *14*, 17. (b) Lange, B. A.; Libson, K.; Deutsch, E.; Elder, R. C. *Inorg. Chem.* **1976**, *15*, 2985.

(13) See, for example: Elder, R. C.; Kennard, G. J.; Payne, M. D.; Deutsch, *Inorg. Chem.* **1978**, *17*, 1296.

(14) Orhanovic, M.; Po, H. N.; Sutin, N. *J. Am. Chem. Soc.* **1968**, *90*, 7224.

(15) See, for example: (a) Dwyer, F. P. J.; Gill, N. S.; Gyarfas, E. C.; Lions, F. *J. Am. Chem. Soc.* **1952**, *74*, 4188. (b) Yamamoto, Y.; Tsukuda, S. *Bull, Chem. Soc. Jpn.* **1985**, *58*, 1509. (c) Chakraborty, P.; Chandra, S. K.; Chakravorty, A. *Inorg. Chem.* **1994**, *33*, 4959.

(16) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

(17) (a) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673. (b) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639.

(18) (a) Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3769. (b) Linck, R. G. *Inorg. Chem.* **1970**, *9*, 2529.

(19) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318.

(20) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

(21) Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 1103.

(22) Shaw, E.; Espenson, J. H. *Inorg. Chem.* **1968**, *7*, 1619.

(23) (a) Singh, A. N.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 1232. (b) Singh, A. N.; Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 655. (c) Ghosh, M. C.; Gould, E. S. *Inorg. Chim. Acta,* **1994**, *225*, 297.

(24) The addition of CH_3CN confers a further advantage in the reductions by $Ru(NH_3)_6{}^{2+}$. This nitrile acts as a scavenger for the more reactive reducing ion $Ru(NH_3)_5H_2O^{2+}$, which may be formed in part during pretreatment of the Ru(II) preparations. See, for example: Rajasekar, N.; Srinivasan, V. S.; Singh, A. N.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 3245.

(25) Dickson, P. N.; Margerum, D. W. *Anal. Chem.* **1986**, *58*, 3153.

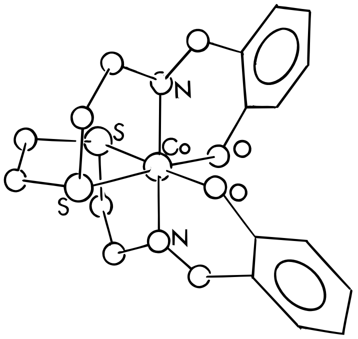
(26) Chen, J. C.; Gould, E. S. *J. Am. Chem. Soc.* **1973**, *95*, 5539.

The oxidation of the *N*-methyldihydrophenazinium ion by the $Co^{III}(N_4O_2)$ complex was monitored at 644 nm, an absorption peak ($\epsilon = 1.4 \times 10^3\ M^{-1}\ cm^{-1}$)[23b] of the methylphenazinium radical, the 1 e^- oxidation product of the reductant used. The analogous oxidation by the $Co^{III}(N_2S_2O_2)$ complex was too rapid to follow, even using stop flow.[27]

Characterization of the Products from the Cr(II) Reactions. A reaction mixture containing 0.040 mol each of the Co(III) complex of the N_4O_2 ligand, **IV**, and Cr^{2+} in 0.10 M $HClO_4$ was allowed to stand 15 min and then passed through a 12 cm column of Biogel P-2 (200−400 mesh). The colored product, a single yellow-green band, was eluted with water and an aliquot oxidized, using H_2O_2 and NaOH,[28] to estimated total chromium as CrO_4^{2-} ($\epsilon_{370} = 4.94 \times 10^3\ M^{-1}\ cm^{-1}$). UV−vis: λ_{max} 560 ($\epsilon = 30\ M^{-1}\ cm^{-1}$), 403 nm ($\epsilon = 1.4 \times 10^3$). This fraction contained 82% of the chromium taken. An analogous treatment of equimolar mixtures of the Co(III) complex of the $N_2S_2O_2$ ligand (III) and Cr^{2+} yielded a green Cr(III) product with maxima at 660 ($\epsilon = 145$) and 398 nm ($\epsilon = 3.4 \times 10^3$). Recovery of chromium Cr in this case was 89%.

Results and Discussion

Determination of the crystal structure of the cobalt(III) complex of the $N_2S_2O_2$ ligand (III)[15c] shows it to be **VI**, in which each O−N−S sequence spans meridional positions (S trans to O) rather than facial sites. NMR examination of the corresponding N_4O_2 complex[15b] supports an analogous mode of coordination in that derivative.



VI

The approach to quantitative yield of Co(II) when the oxidant is taken in excess (Table 2) indicates that we are dealing in each case with a straightforward le^- transaction between metal centers. The slight departures from 1:1 stoichiometry appear to be random and probably reflect partial consumption of the added reductant by traces of oxygen, especially since the uncomplexed ligands have been shown to be inert to those reductants under the reaction conditions employed.

Neither Co(III) derivative gives $Cr(H_2O)_6^{3+}$ as a preponderant oxidation product on reaction with Cr^{2+}. Electronic spectra of both resulting Cr(III) species feature strong absorbance in the near ultraviolet characteristic of the salicyldimine function, and that from reduction of the $O_2S_2N_2$ chelate exhibits a peak at 660 nm ($\epsilon = 145\ M^{-1}\ cm^{-1}$), which may be taken to be indicative of a Cr(III)−S linkage.[29] If we assume this to be the primary oxidation product, we may conclude that this electron transfer has proceeded through a Cr(II)−S−Co(III) precursor. The low energy maximum at 560 nm in the Cr(III) spectrum obtained from reduction of $Co^{III}N_4O_2$ appears to be consistent with a O_6-bound product of the type Ar−O−$Cr^{III}(H_2O)_5$, rather than a complex in which donor nitrogen occupies one or more coordination sites.[4]

Table 3. Rate Constants for Reductions of Cobalt(III) Complexes of $N_2S_2O_2$- and N_4O_2-Coordinating Ligands, **III** and **IV**[a]

	k, $M^{-1}\ s^{-1}$, 25 °C	
reductant	$[Co^{III}(N_2S_2O_2^{2-})]^+$	$[Co^{III}(N_4O_2^{2-})]^+$
Cr^{2+}	2.4×10^4	$12 + 44[H^+]$[b]
$Ru(NH_3)_6^{2+}$[c]	4.5×10^2	0.045
Eu^{2+}	1.5×10^4	$0.023 + 0.002[H^+]^{-1}$[b]
V^{2+}	5.3×10^2	0.18
Ti^{III}[c]	$0.10[H+]^{-1}$[b]	$\leq 3 \times 10^{-4}$
Cu^+	0.06	≤ 0.01
N-Methyldihydro-phenazine(V)[d]	$\geq 3 \times 10^6$	1.6×10^4[b]

[a] Reactions were carried out at $\mu = 0.10$ M ($HClO_4$) unless otherwise indicated. Reductions of $[Co^{III}(N_2S_2O_2^{2-})]^+$ (chelate **V**) were run in 98/2 H_2O−CH_3CN (see Experimental Section). [Red] = 0.001 − 0.060 M, [Ox] = (1.0−24.0) × 10^{-4} M. [b] $\mu = 1.0$ M; $[H^+] = 0.20$−1.0 M. [c] Reactions in chloride medium. [d] Reactions in triflate medium.

Rate constants for reductions of the Co(III) complexes of ligands **III** and **IV** are summarized in Table 3. Among the reactions of the metal-center reductants, only the reductions of Co(III)−N_4O_2 with Cr(II) and Eu(II), and that of Co(III)−$N_2S_2O_2$ with Ti(III), exhibit perceptible rate variation with $[H^+]$, and these were examined at $\mu = 1.0$ M to allow inclusion of a wider range of acidity.

The $[H^+]^{-1}$-proportionality found for the $Co(N_2S_2O_2)$−Ti^{III} reaction tells us that, as with many known reductions by Ti(III),[30] the active reducing species here is the deprotonated cation, $Ti(OH)^{2+}$. The tabulated value, in combination with the reported pK_A of Ti^{3+}(aq) 2.8,[31] yields $k_{Ti(OH)} = 60\ M^{-1}\ s^{-1}$ (25 °C, $\mu = 1.0$ M).

Assignment of inner-sphere paths to both reductions by Cr^{2+}, besides being dictated by the observed transfer of the cobalt-bound ligand to the Cr(III) product, is in accord with the magnitude of their rate constants (see below) and with the appearance of a substantial $[H^+]$-proportional kinetic term in the case of the N_4O_2-bound oxidant. This term may be taken to be diagnostic of redox bridging[17b,32] and has been attributed to an easing of electron passage through the mediating group in response to protonation of a donor center lying apart from the bridging function. Although this type of acidity pattern has been considered characteristic of carbonyl-substituted systems, it almost certainly results from partial protonation of a cobalt-bound imine nitrogen in this instance.

In view of the substitution-inert character of $Ru(NH_3)_6^{2+}$, reductions with this cation may be assumed, with confidence, to be outer-sphere. Moreover, the recognized[18a,33] upper limit (near 100 $M^{-1}\ s^{-1}$) on inner-sphere V^{2+} rates imposed by slow substitution at the d^3 center requires that the V^{2+} reduction of the $Co^{III}S_2$ complex ($k = 530\ M^{-1}\ s^{-1}$) be predominantly outer-sphere as well. The reported[20] approaches to constant outer-sphere reactivity ratios pertaining to the several dispositive reductants taken (k_{Ru}:k_V:k_{Eu}:k_{Cr} = 200:70:20:1) enable us to draw (with caution)[34] additional mechanistic inferences.

---

(27) Similar experiments were attempted using the dihydro derivative of riboflavin.[23a] Approximate second order rate constants for the oxidation of this species by the $Co^{III}(N_4O_2)$ complex were 62 $M^{-1}\ s^{-1}$ in 1.1 M H^+ and 40 $M^{-1}\ s^{-1}$ in 0.2 M H^+ (25 °C, $\mu = 1.1$ M). Reactions with the $N_2S_2O_2$ complex yielded kinetic curves that could not be interpreted.

(28) See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand., Sect. A* **1952**, *48*, 41.

(29) See, for example: Weschler, C. J.; Deutsch, E. *Inorg. Chem.* **1973**, *12*, 2682.

(30) See, for example: (a) Orhanovic, M.; Earley, J. E. *Inorg. Chem.* **1975**, *14*, 1478. (b) Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1975**, *14*, 873. (c) Thompson, G. A. K.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 638. (d) Hery, M.; Wieghardt, K. *Inorg. Chem.* **1978**, *17*, 1130.

(31) Krentzien, H.; Brito, F. *Ion (Madrid)*, **1970**, *14*; *Chem. Abstr.* **1970**, *73*, 7865.

(32) (a) Zanella, A.; Taube, H. *J. Am. Chem. Soc.* **1972**, *94*, 6403. (b) Gould, E. S. *J. Am. Chem. Soc.* **1974**, *96*, 2373.

(33) Baker, B. R.; Orhanovic, M.; Sutin, N. *J. Am. Chem. Soc.* **1967**, *89*, 722.

(34) Gould, E. S. *Inorg. Chem.* **1979**, *18*, 900.

Since outer-sphere reductions by Eu^{2+} proceed an order of magnitude more slowly than those by $Ru(NH_3)_6^{2+}$, the observed very rapid Eu^{2+} reduction of our sulfur oxidant must (as is the case with Cr^{2+}) be preponderantly inner-sphere, and similar reasoning leads to the same conclusion for the V^{2+} reduction of the N_4O_2 complex.[35] The rate for the $Co^{III}(N_4O_2)-Eu^{2+}$ reaction is consistent with partition between the two paths, with the outer-sphere route ($k_{OS} \sim 5 \times 10^{-3}$) contributing about 20% of the total. The observed inverse-[H^+] term for this reaction is in accord with a substantial bridged component.[17b]

The *N*-methyldihydrophenazinium cation, like other related dihydroflavinoid systems,[23b] has been shown to reduce a variety of Co(III) complexes by an outer-sphere process. Rate constants are generally several orders of magnitude greater than those for $Ru(NH_3)_6^{2+}$, a selectivity which pertains also to the present systems. As with the metal-center reductants, the $Co^{III}S_2$ oxidant exhibits greatly enhanced reactivity in relation to its N_4O_2-bound analog, with reduction of chelate **V** too rapid to measure with our methods.

The most striking aspect of the present study is obviously the persistence of the marked kinetic advantage in reductions of the $N_2S_2O_2$-bound over the N_4O_2-bound oxidants. Rate ratios of 10^3-10^6 are observed although variations in the nature of the reductant may be reflected in alteration of the rate law and a change in the predominant reaction path. Enhanced rates with the sulfur-bound oxidant appear to extend even to metal-free coreagents.

It is difficult to escape the conclusion that rate increases associated with sulfur-containing ligands arise from more than one effect. The structural trans effect in redox reactions, as formulated originally by Orgel,[36] and applied specifically to S-bonded Co(III) oxidants by Elder,[8] pertains to inner-sphere reactions in which rate enhancement is associated with attack at a bridging site, lying trans to donor sulfur, which is attached by a stretched metal-to-ligand bond. This description may be applicable to the high reduction rates for Eu^{2+}, V^{2+}, and $Ti(OH)^{2+}$, to which we have assigned bridged paths (with the site of attack not determined). The same picture cannot, however, be extended, without modification, to the reduction by Cr^{2+} in this study, for here redox bridging occurs at the ligating sulfur itself rather than at the position trans to it. Moreover, the model appears to be quite inappropriate for the outer-sphere reductions by $Ru(NH_3)_6^{2+}$ and by the dihydrophenazinium cation, both of which likewise proceed at greatly elevated rates.

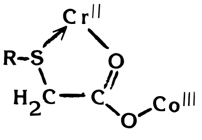
If we instead adopt the view that the principal accelerative feature resulting from sulfur ligation depends neither on mechanism nor, for bridged reactions, on the point of attack, we may note that substantial electron drift from the very polarizable sulfur atoms to the Co(III) center in chelate **VI** imparts considerable covalency to the S−Co bonds.[37] Since there are, in addition, low-lying 3d orbitals one each sulfur, the $(S)_2Co^{III}$ arm of the oxidant has taken on the character of a quasiaromatic fragment. The incorporation of metal centers into delocalized electron systems almost invariably facilitates electron transfer,[38] presumably because lengthening and shrinking of metal−ligand bonds associated with changes in oxidation state, which contribute substantially to the Franck−Condon barrier to these changes, become minimized in such systems.[39]

Table 4. Specific Rates for Reductions of Cobalt(III) Complexes, $[RCH_2CO_2Co[NH_3)_5]^{2+}$ (25 °C), and Effect of α-Thio Substitution[a]

		k, M^{-1} s^{-1}			
reductant	μ, M	R = H (**I**)	R = $C_6H_5CH_2S$ (**II**)	k_{II}/k_I	ref
Cr^{2+}	1.5	0.35	5.2	15	4
V^{2+}	1.0	1.25	1.64	1.3	20
Eu^{2+}	1.0	1.7	1.84	1.1	17b
Ti(III)	1.0[b,c]	0.045	0.010	0.22	*e*
Cu^+	1.1	0.004	0.070	18	16
$Ru(NH_3)_6^{2+}$	0.50[c,d]	0.022	0.041	1.9	20
N-methyldihydrophenazinium (**V**)	1.0	0.057	0.018	0.31	*e*

[a] Reactions were run in ClO_4^- media with [H^+] = 1.0 M unless otherwise indicated. [b] [H^+] = 0.20 M. [c] Supporting electrolyte was Cl^-. [d] [H^+] = 0.013 M. [e] This work.

The source of the (less striking) augmentation of k_{Cr} values for the α-thio-substituted carboxylato complexes such as **II** must lie elsewhere, for sulfur in these oxidants is situated outside the coordination sphere of Co(III). These rate increases were originally ascribed[4] to a greater degree of conversion of the reactants to the binuclear precursor, **VII**, reflecting S−Cr(II) chelation, for they are not observed[20] with the outer-sphere reductant $Ru(NH_3)_6^{2+}$. It was not clear, however, why the analogous α-alkoxy complexes (in which oxygen replaces "side-chain" sulfur) exhibit no such enhancements.[40] We suspect that precursors of type **VII** receive an extra measure of stabilization from chromium-to-sulfur back-bonding involving interaction of the single e_g electron of the d^4 center with a low-lying but empty d-orbital of sulfur. A similar effect would be expected in comparisons of reduction rates by the d^{10} cation, Cu^+, and indeed k_{Cu} for the S-substituted complex, **II**, is found to be greater than 17 times that for the acetato complex, **I**.[16] Moreover, the suggested picture is in keeping with the absence of acceleration by pendant α-alkylthio groups in reductions by Ti(III), by V(II) (both of which centers are devoid of e_g electrons) and by the f^7 species Eu(II) (Table 4), although each of these reductants, and the outer-sphere reagent $Ru(NH_3)_6^{2+}$ as well, is seen, in the present study, to respond dramatically to incorporation of sulfur in the primary coordination sphere of the oxidant.



VII

Acknowledgment. We are pleased to thank Dr. Partha Basu for help in preparing figures and Mrs. Arla McPherson for technical assistance.

IC950870V

---

(35) The data of Thompson and Sykes[30c] lead to the relationship (1), which compares, in approximate fashion, rates for outer-sphere reductions

$$\log k_{Ti} = 0.40(\log k_{Ru}) - 3.8 \tag{1}$$

by Ti(III) in 1 M H^+ to those for the corresponding reductions by $Ru(NH_3)_6^{2+}$ in 0.001−0.10 M H^+. This, in conjunction with k_{Ru} for $Co(N_2S_2O_2)$, leads to an estimated outer-sphere rate constant 2×10^{-3} M^{-1} s^{-1} for k_{Ti}, i.e., a value 1/50th of that observed. Hence, a large inner-sphere contribution is likely here as well.

(36) See, for example: Earley, J. E. *Prog. Inorg. Chem.* **1970**, *13*, 243.

(37) See, for example: (a) Tanabe, Y.; Sugano, S. *J. Phys. Chem. Jpn.* **1954**, *9*, 753, 766. (b) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; 2nd ed.; Wiley: New York, 1968; p 113.

(38) See, for example: Lappin, A. G. *Redox Mechanisms in Inorganic Chemistry*; Ellis Horwood: New York, 1994; p 79.

(39) For detailed discussions concerning relationships between differences in bond lengths and electron transfer rates, see: (a) Friedman, H. L.; Newton, M. D. *Faraday Discuss. Chem. Soc.* **1982**, *74*, *73*. (b) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.

(40) Butler, R. D.; Taube, H. *J. Am. Chem. Soc.* **1965**, *87*, 5597.