and the C–O distance of 1.10 (1) Å is short (typically 1.14–1.17 Å).[22-23,27] The Rh–C–O angle of 174.7 (7)° indicates a slight deviation from linearity. These unusual values may be due to steric interaction between the CO ligand and the phenyl *o*-H atoms (vide supra) or due to some inadequacy in the refinement. Distances and angles within the phenyl rings are normal, and all of the rings are planar within experimental error. The large thermal parameters and the large differences in equivalent distances and angles within the BF_4^- anion suggest some disorder. However, an obvious disordered model was not apparent in the final difference Fourier map. The average B–F distance (1.29 (2) Å) and F–B–F angle (108 (2)°) are well within the range of accepted values.

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Registry No. $[Rh(dppm)_2CO]BF_4$, 73574-66-0; $[Rh(dppp)_2CO]BF_4$, 73610-24-9; $[Rh(dppm)_2]BF_4$, 53450-78-5; $[Rh(dppp)_2]BF_4$, 70196-21-3; $Rh_2Cl_2(COD)_2$, 12092-47-6.

Supplementary Material Available: Table II (root-mean-sqaure amplitudes of thermal vibration) and a listing of observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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Kinetics of Reduction of Metal Complexes by Dithionite

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Dithionite is used extensively for the reduction of proteins, and there have been recently a number of kinetic studies of these reactions.[2] By contrast, there have been limited investigations of reactions of dithionite with metal complexes.[3-5] One of the very interesting features of dithionite ion is its ability to reduce as the intact $S_2O_4^{2-}$ ion and/or via the dissociated anion radical SO_2^-.[3] We report here on the reduction of 11 cobalt(III) complexes of a variety of types, as well as the $Fe(EDTA)^-$ and $Mn(CyDTA)^-$ ions.[6]

Experimental Section

Complexes were prepared by literature methods (see Table I).[7-21]

Table I. Activation Parameters for Reduction by $S_2O_4^{2-}$ (k_2) and SO_2^- (k_3) Ions at 25 °C, pH 7.0, and $I = 0.4$ M

complex ion[a]	k_2, $M^{-1}\,s^{-1}$	k_3,[b] $M^{-1}\,s^{-1}$	$\Delta H^{\ddagger}$,[c] kcal mol^{-1}	$\Delta S^{\ddagger}$,[c] eu
cis-$Co(IDA)_2^-$ [7,8]	1.9	$\leq 10^3$	15.4	−6
trans-$Co(IDA)_2^-$ [7,8]	1.6	$\leq 10^3$	14.0	−11
$Co(EDTA)^-$ [9]	≤ 0.1	1.0×10^3	17.4	−7
	≤ 0.1	1.3×10^3 [d]		
$Co(CyDTA)^-$ [10]	≤ 0.1	2.3×10^3		
$Co(EDTA)Cl^{2-}$ [11]	<10	2.1×10^5	15.5	−3
$Co(MEDTA)Br^-$ [12,13]	$\leq 10^2$	6.5×10^6 [e]	13.0[e]	−4[e]
	≤ 0.1	1.3×10^4 [f]	10.5[f]	−24[f]
$Co(MEDTA)OH_2$ [12,13]	≤ 0.4	1.5×10^4		
$Co(C_2O_4)_3^{3-}$ [14]	≤ 0.4	1.8×10^4	14.9	−9
		1.0×10^4 [d]		
$[Co(C_2O_4)_2OH]_2^{4-}$ [15,16]	≤ 0.1	1.6×10^4	18.4	+2
$[Co(NTA)OH]_2^{2-}$ [17,18]	≤ 0.1	4.6×10^3		
$Co(terpy)_2^{3+}$ [14]	4.3×10^5	$\leq 10^7$	17.0	+24
$Fe(EDTA)^-$ [20]	3.6×10^4	$\leq 2 \times 10^6$	13.7	+8
$Mn(CyDTA)^-$ [21]	2.1×10^6	$\leq 10^8$		

[a] Abbreviations are listed in ref 6, and references to preparation are superscripted. [b] Calculated from experimental value of $K_1^{1/2}k_3$ with $K_1 = 1.4 \times 10^{-9}$ M.[3] [c] Activation parameters from either $\log k_2$ or $\log (K_1^{1/2}k_3)$ vs. $1/T$ plot. $\Delta H^{\ddagger} = \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = \pm 3$ eu are the approximate errors for most systems. [d] pH ~10.0. [e] Fast reacting component. [f] Slow reacting component.

The kinetics were studied by using a Beckman 24 spectrophotometer or a Gibson-Durrum stopped-flow apparatus, and serum cap sealed cells and anaerobic conditions were maintained throughout the experiments. The reactions of the cobalt(III) complexes (100 μM–2.0 mM) with dithionite (1–30 mM) were examined in the 530–600-nm region. For the rapid reactions of the $Co(terpy)_2^{3+}$, $Fe(EDTA)^-$, and $Mn(CyDTA)^-$ ions, 10–100 μM complex and 50 μM–4 mM dithionite were employed with observations at 450, 400, and 510 nm, respectively. Two rates, easily separable, were obtained with the isomeric mixture[13] in $Co(MEDTA)Br^-$. Changes in wavelength or concentrations of complex were without effect on the pseudo-first-order rate constants measured. The majority of the studies were at 25.0 °C, pH 7.0 (maintained with TRIS) and $I = 0.4$ M. Full kinetic data are contained in Table II.[22]

Results

Spectral examination of the products of reduction by dithionite indicated formation of the corresponding bivalent metal ion complex(es). The kinetic scheme in eq 1–3 can be

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^- \quad K_1, \text{ rapid} \tag{1}$$

$$M(III) + S_2O_4^{2-} \rightarrow M(II) + S(IV) \quad k_2 \tag{2}$$

$$M(III) + SO_2^- \rightarrow M(II) + S(IV) \quad k_3 \tag{3}$$

applied to dithionite reduction of the complexes (designated M(III)) for which the rate law (4) applies. With all com-

$$\text{rate}/[M(III)] = k_{obsd} = k_2[S_2O_4^{2-}] + k_3K_1^{1/2}[S_2O_4^{2-}]^{1/2} \tag{4}$$

plexes examined,[23] plots of either k_{obsd} vs. $[S_2O_4^{2-}]$ or k_{osbd} vs.

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[1] On leave from Department of Chemistry, University of Jodhpur, Jodhpur India.
[2] P. C. Harrington, D. J. A. deWaal, and R. G. Wilkins, *Arch. Biochem. Biophys.*, **191**, 444 (1978), and references therein.
[3] D. O. Lambeth and G. Palmer, *J. Biol. Chem.*, **248**, 6095 (1973).
[4] R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, **14**, 866 (1975).
[5] J. C. Cassatt, M. Kukuruzirska, and J. W. Bender, *Inorg. Chem.*, **16**, 3371 (1977).
[6] Abbreviations: IDA = iminodiacetate; EDTA = ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate; CyDTA = *trans*-1,2-cyclohexanediamine-*N*,*N*,*N'*,*N'*-tetraacetate; MEDTA = *N*-methylethylenediamine-*N*,*N'*,*N'*-triacetate; NTA = nitrilotriacetate, terpy = 2,2',2''-terpyridine.
[7] J. Hidaka, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **35**, 567 (1962).
[8] R. A. Rader and D. R. McMillin, *Inorg. Chem.*, **18**, 545 (1979).
[9] F. P. Dwyer, E. C. Gyarfas, and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).
[10] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).
[11] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **80**, 4480 (1958).
[12] C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **7**, 1393 (1968).
[13] M. H. Evans, B. Grossman, and R. G. Wilkins, *Inorg. Chim. Acta*, **14**, 59 (1975).
[14] J. C. Bailar, Jr., and E. M. Jones, *Inorg. Synth.*, **1**, 37 (1939).
[15] A. W. Adamson, H. Ogata, J. Grossman, and R. Newbury, *J. Inorg. Nucl. Chem.*, **6**, 319 (1958).
[16] L. Hin Fat and W. C. E. Higginson, *J. Chem. Soc. A*, 298 (1967).
[17] M. Mori, M. Shibata, E. Kyuno, and Y. Okubo, *Bull. Chem. Soc. Jpn.*, **31**, 940 (1958).
[18] D. R. Meloon and G. M. Harris, *Inorg. Chem.*, **16**, 434 (1977).
[19] B. R. Baker, F. Basolo, and H. M. Neumann, *J. Phys. Chem.*, **63**, 371 (1959).
[20] H. J. Schugar, A. T. Hubbard, F. C. Anson, and H. B. Gray, *J. Am. Chem. Soc.*, **91**, 71 (1969).
[21] R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, **6**, 139 (1967).
[22] Supplementary material.

0020-1669/80/1319-2177$01.00/0

$[S_2O_4^{2-}]^{1/2}$ were linear with zero intercepts, indicating sole contribution to the rate of either the first or second term in (4), respectively. The slopes equaled k_2 or $k_3K_1^{1/2}$, respectively, and with use of a value for $K_1 = 1.4 \times 10^{-9}$ M at 25 °C[3] k_3, the rate constant for reaction of SO_2^-, could be calculated. Values are given in Table I. By plotting $k_{osbd}/S_2O_4^{2-}]^{1/2}$ vs. $[S_2O_4^{2-}]^{1/2}$ or $k_{obsd}/[S_2O_4^{2-}]$ vs. $[S_2O_4^{2-}]^{-1/2}$, it was possible from the intercepts to deduce a maximum likely contribution of k_3 or k_2, respectively, to the dominant path. These higher limits are included in Table I.

The variation of k_2 with temperature leads directly to values of $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ for reaction of $S_2O_4^{2-}$ (Table I). If the second term in (4) is dominant, then the usual Arrhenius plot of log $(k_{osbd}/[S_2O_4^{2-}]^{1/2})$ vs. $1/T$ will yield $\Delta H^\ddagger_{osbd}$ and $\Delta S^\ddagger_{obsd}$ values (Table I). These however are composite quantities, equaling $(1/2\Delta H_1 + \Delta H_3^\ddagger)$ and $(1/2\Delta S_1 + \Delta S_3^\ddagger)$ respectively. The values of ΔH_1 and ΔS_1 for the dissociation of dithionite can be estimated as +7.3 kcal mol^{-1} and −19 eu, respectively, from the temperature variation of K_1 deduced from EPR measurements.[24] Thus the values of $\Delta H_3^\ddagger$ and $\Delta S_3^\ddagger$ for reaction of SO_2^- are some 3.7 kcal mol^{-1} *lower* and 9 eu more *positive* than the values given for $\Delta H^\ddagger_{osbd}$ and $\Delta S^\ddagger_{obsd}$ in Table I, and this should be borne in mind in the discussion.

Discussion

The following features emerge from this study.

(a) Eight of the eleven cobalt(III) complexes are reduced solely by SO_2^- in the conditions used, and for the remaining three reduction by SO_2^- may not be unduly sluggish, but this path is swamped by that involving direct $S_2O_4^{2-}$ reduction. Indeed with $Co(terpy)_2^{3+}$, Fe(EDTA)$^-$, and Mn(CyDTA)$^-$ complexes which are rapidly reduced by $S_2O_4^{2-}$, it will be difficult to detect any contribution from an SO_2^- reaction, since the concentration of SO_2^- will be ~1 μM when $S_2O_4^{2-}$ is 1 mM and the rate constant for SO_2^- will therefore need to approach 10^7–10^8 M^{-1} s^{-1} for its contribution to be registered. Examination of Table I shows that generally $\Delta H^\ddagger$ values are smaller for reactions involving SO_2^- than for those with $S_2O_4^{2-}$.

(b) The reactivity order $e_{aq}^- > CO_2^- > SO_2^-$ holds for reaction of these radicals with a number of iron proteins.[25] This sequence holds also for cobalt(III) complexes, rate constants for reduction of a number of complexes $Co(NH_3)_5X^{2+}$ by CO_2^- being in the range 4×10^7 to 1.9×10^9 M^{-1} s^{-1}.[26] Although CO_2^- shows more selectivity than does e_{aq}^-, the range displayed by SO_2^- is wider still, varying from 10^3 to 6.5×10^6 M^{-1} s^{-1} (Table I). The second-order rate constants for reaction of Fe(EDTA)$^-$ with e_{aq}^-, CO_2^- and SO_2^- are 2.3×10^{10}, 5×10^7,[27] and $\leq 2 \times 10^6$ M^{-1} s^{-1} respectively. The observed reactivity sequence may be related to reduced reductant power ($E° =$ −2.8, −2.0,[28] and −0.7 V[29] for e_{aq}^-, CO_2^-, and SO_2^-, respectively).

(c) All the anticipated absorption changes in the reductions of the dimers are uniphasic first-order processes. Consequently, the slow one-electron reduction by SO_2^- of one Co(III) in either dimer must be followed by either a similar or (more likely) much faster reduction of the other Co(III) center. There have been few reported studies of the reduction of dimeric complexes. The slow/fast sequence is observed for the two-electron reductions of some μ-(dihydroxydicarboxylate) cobalt(III) complexes.[30]

(d) It seems reasonable to regard these reactions as outer sphere since they are generally more rapid than cobalt(III)–ligand bond rupture is likely to be. Although it can be considered dangerous to apply Marcus' theory[31] to these reactions with a large driving force,[32] nevertheless it is an interesting exercise to consider from this viewpoint the rate constants for reaction of SO_2^- with a number of the complexes. The rate constant k_{12} for the reaction between the complex and SO_2^- is related to k_{11} and k_{22}, the self-exchange rate constants for the SO_2^-/SO_2 and M(III)/M(II) couples, and K_{12}, the equilibrium constant for the reaction, by the relationship (5). k_{22} is known for the CoEDTA$^{-/2-}$ (4×10^{-7} M^{-1} s^{-1}), $Co(C_2O_4)_3^{3-/4-}$ (2×10^{-7} M^{-1} s^{-1}), MnCyDTA$^{-/2-}$ (1 M^{-1} s^{-1}), and Fe(EDTA)$^{-1/2-}$ (3×10^4 M^{-1} s^{-1}) couples,[33] and K_{12} can be calculated from the oxidation potentials for the metal complexes (+380, +570,[16] +820, and +120 mV, respectively[33]) as well as for the HSO_3^-/SO_2 couple (−660 mV at pH 7).[29] Using our experimentally determined k_{12} values for reaction of the two Co(III) complexes with SO_2^- leads to a self-consistent k_{11} value of 10^{-3} M^{-1} s^{-1}. Applying this value to the Mn(CyDTA)$^-$ and Fe(EDTA)$^-$ reactions with SO_2^- yields k_{12} ~10^8 and ~10^6 M^{-1} s^{-1}, respectively, values at least consistent with the lower limits determined experimentally. Subtleties in the reductions by $S_2O_4^{2-}$ are indicated by the observation of its similar reactivity toward *cis*- and *trans*-Co(IDA)$_2^-$ in spite of their widely differing potentials (+360 and ≤170 mV, respectively[8]). Although *cis*-Co(IDA)$_2^-$ and Co(EDTA)$^-$ are structurally extremely similar and have identical spectra and oxidation potentials (and possibly a similar reactivity toward SO_2^-), the reaction of $S_2O_4^{2-}$ is at least 20 times greater with the IDA than the EDTA complex. It appears that dithionite is an interesting reducing agent which bears further kinetic examination in its reduction of metal complexes.[34]

$$k_{12}^2 = k_{11}k_{22}K_{12}f_{12}$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/10^{22})} \qquad (5)$$

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Registry No. *cis*-Co(IDA)$_2^-$, 21718-59-2; *trans*-Co(IDA)$_2^-$, 33848-79-2; Co(EDTA)$^-$, 15136-66-0; Co(CyDTA)$^-$, 20080-68-6; Co(EDTA)Cl^{2-}, 23467-31-4; Co(MEDTA)Br$^-$, 56336-75-5; Co(MEDTA)OH$_2$, 33972-19-9; $Co(C_2O_4)_3^{3-}$, 15053-34-6; $[Co(C_2O_4)_2OH]_2^{4-}$, 33887-54-6; $[Co(NTA)OH]_2^{2-}$, 56930-89-3; $Co(terpy)_2^{3+}$, 19137-07-6; Fe(EDTA)$^-$, 15275-07-7; Mn(CyDTA)$^-$, 73360-48-2; $S_2O_4^{2-}$, 14844-07-6; SO_2^-, 12143-17-8.

Supplementary Material Available: Table II, raw kinetic data for reduction by dithionite ion (5 pages). Ordering information is given on any current masthead page.

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(23) There was an indication of curvature (concave down) in the $k_{obsd}/[S_2O_4^{2-}]$ plot for Fe(EDTA)$^-$ at 25 °C. This could indicate a contribution from an SO_2^- reduction path. However the absence of deviation from linearity of the $k_{osbd}/[S_2O_4^{2-}]$ plot at lower temperatures (where rates are slower and more precisely measured) suggests sole reduction by $S_2O_4^{2-}$.

(24) F. E. J. Wood, Ph.D. Thesis, University of Arizona, 1974.

(25) P. C. Harrington and R. G. Wilkins, *J. Biol. Chem.*, **254**, 7505 (1979).

(26) M. Z. Hoffman and M. Simic, *Inorg. Chem.*, **12**, 2471 (1973).

(27) Y. A. Ilan and G. Czapski, *Biochim. Biophys. Acta*, **498**, 386 (1977).

(28) J. Lilie, G. Beck, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **75**, 458 (1971).

(29) S. G. Mayhew, *Eur. J. Biochem.*, **85**, 535 (1978).

(30) I. Baldea, K. Wieghardt, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 78 (1977).

(31) R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 21 (1960); *J. Phys. Chem.*, **67**, 853 (1963).

(32) M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **99**, 5615 (1977).

(33) R. G. Wilkins and R. E. Yelin, *Inorg. Chem.*, **7**, 2667 (1968), and references cited.

(34) After this work was submitted, a paper appeared on the reduction of several pentaaminecobalt(III) complexes by dithionite (D. Pinnell and R. B. Jordan, *Inorg. Chem.*, **18**, 3191 (1979)). Reduction by either SO_2^- or $S_2O_4^{2-}$ or both together was observed, and in certain systems, a bridging mechanism was proposed.