failure to detect a signal of a Mo atom with oxidation state less than VI, here $Mo^{A,A'}$, under conditions where those of tetrahedral Mo(VI) are readily observed, has been recorded previously.[3,41] This effect presumably results from quadrupolar line broadening owing to a strongly noncubic environment. The relative intensities of the $Mo^{C,C'}$ signals support the presence of essentially equimolar quantities of the two anions in the preparative sample. In the ^{17}O NMR spectrum, the chemical shifts of $O^{B,B'}$ in common fragment a would be expected to be nearly identical, leading to the assignment of the 802 and 804 ppm features to these sites.[42] Because ^{17}O NMR resonances at tetrahedral Mo(VI) become progressively deshielded as the number of sulfide ligands increases, the 850 ppm signal is ascribed to O^C of fragment e. The remaining resonances at 813 and 820 ppm are assigned to $O^{A,A'}$, whose environments are resolvably differentiated by the terminal ligands in fragments e and f. Other than the result for **3**,[42] we are unaware of previous data for ^{17}O NMR chemical shifts of $Mo^{IV,V}{=}O$ units. At least for **3**, $[Mo_3S_8O_2]^{2-}$, and $[Mo_3S_7O_3]^{2-}$, these shifts fall into the same interval associated with $Mo^{VI}{=}O$ groups of polyoxoanions.[3,27]

Summary. Reaction of an $\alpha:\beta \sim 7:1$ isomeric mixture of $[Mo_8O_{26}]^{4-}$ in acetonitrile with 1–8 equiv of $(Me_3Si)_2S$ resulted in cleavage of the cage structures **1** and **2**. A significant extent of cage fracture was observable even at 1–2 equiv, in which the systems $[MoO_3(OSiMe_3)]^-$ and $[MoO_2S(OSiMe_3)]^-$ were formed in appreciable amounts. Both isomers were essentially absent in the 8-equiv system, which exhibited a series of new ^{17}O NMR signals. On a preparative scale this system afforded a diamagnetic crystalline n-Bu_4N^+ salt containing virtually equimolar amounts of $[Mo_3S_8O_2]^{2-}$ and $[Mo_3S_7O_3]^{2-}$. The formation of trinuclear products discouraged a study of reaction systems with >8 equiv of the sulfide reagent. The two anions contain a set of structural fragments not previously assembled in a single molecule. The oxidation state description $[(S_2)Mo^{VI}O(\mu\text{-}S)_2Mo^{IV}O(\mu\text{-}S)_2Mo^{VI}S(S/O)]^{2-}$ is offered, and assignments of the ^{17}O and ^{95}Mo NMR spectra are proposed. The species $[MoOS_8]^{2-}$, $[Mo_2S_6O_2]^{2-}$ (**3**), $[Mo_2S_7O_4]^{2-}$ (**4**), $[Mo_3OS_8]^{2-}$ (**5**), $[Mo_3S_8O_2]^{2-}$, and $[Mo_3S_7O_3]^{2-}$ constitute the current set of characterized oxothiomolybdates.[43] From the present results and those for $[Mo_2O_7]^{2-}$,[3] the reagent $(Me_3Si)_2S$ is capable of effecting O/S ligand substitution, but with partial reduction to Mo(IV,V) and Mo–O skeletal bond cleavage. It is apparent that the latter events preclude sustenance of a sulfide-substituted version of the initial polyoxoanion structure, at least with $(Me_3Si)_2S$ as the sulfide source. If reduction precedes cage disruption, polyoxotungstates may be more amenable to extensive substitution, provided reduction potentials follow the usual order W < Mo.

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Registry No. **1**, 97295-50-6; **2**, 59054-50-1; $(n\text{-}Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$, 97295-49-3; $(Me_3Si)_2S$, 3385-94-2.

Supplementary Material Available: X-ray crystallographic data for $(n\text{-}Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$ including tables of anisotropic temperature factors for non-hydrogen atoms, positional and isotropic temperature factors for hydrogen atoms, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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(41) Gheller, S. F.; Hambley, T. W.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *J. Am. Chem. Soc.* **1983**, *105*, 1527.

(42) In earlier work we observed that treatment of $[Mo_2S_6O_2]^{2-}$ (**3**) with $^{17}OH_2$ produced a signal at 804 ppm, which was also found in the spectra of the $[Mo_2O_7]^{2-}/(Me_3Si)_2S$ reaction systems.[3] Because **3**, $[Mo_3S_8O_2]^{2-}$, and $[Mo_3S_7O_3]^{2-}$ contain the common fragment a, we cannot exclude the possibility that one or both of the latter anions are (very minor) products of those systems. The occurrence of significant quantities of **3** in the present preparative samples is unlikely on the basis of elemental analysis and the lack of a suitably intense single signal for sites O^B and $O^{B'}$.

(43) $[Mo_5O_{21}S_2]^{4-} = [Mo_5O_{15}(SO_3)_2]^{4-}$ is not included inasmuch as it contains only oxidized sulfur: Matsumoto, K. Y.; Kato, M.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 106.

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Electron Transfer. 74. Reduction of Carboxylato-Bound Chromium(V) with Iron(II). Intervention of Chromium(IV)[1a]

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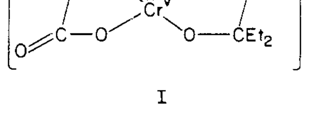
The chelated (carboxylato)chromium(V) anion bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) reacts rapidly with iron(II) at pH 2–4 in aqueous perchlorate, yielding a chromium(III) product, the electronic spectrum and ion-exchange behavior of which correspond to that of a bis-chelated hydroxycarboxylato complex of $(H_2O)_2Cr^{III}$. Reactions in the presence of an excess of the ligand anion, 2-ethyl-2-hydroxybutyrate (Lig^-), are found to pass through a strongly absorbing (λ_{max} 515 nm, $\epsilon = 1.5 \times 10^3$ M^{-1} cm^{-1}) intermediate, the properties of which indicate it to be a complex of the unusual oxidation state Cr(IV). The formation of this intermediate entails a combination of two routes, the first an inverse-[acid] path and the second with a rate proportional to $[Fe(Lig)^+]$. The reduction of the intermediate by excess Fe(II) proceeds at a specific rate $(2.7 \pm 0.4) \times 10^4$ M^{-1} s^{-1} (21 °C, $\mu = 0.50$ M), independent of both $[H^+]$ and $[Lig^-]$. Unlike reductions by N_2H_4 and NH_2OH, the initial reaction with Fe(II) does not require loss of ligand from the Cr(V) complex prior to the redox process. As with reduction by Ti(III), it appears that both steps of the electron-transfer sequence, $Cr^V \rightarrow Cr^{IV} \rightarrow Cr^{III}$, proceed with preservation of the ligand connectivity about chromium, suggesting that the Cr^{IV} intermediate, like the Cr^V reactant, is a bis chelate. Whereas the specific rate for reduction of Cr(IV) by Ti(III) is thought to be at least 15-fold greater than that for reduction of Cr(V) to Cr(IV), rate contants for the corresponding 1e reductions by Fe(II) are more nearly comparable. If the reductions by Ti(III) are taken to be outer sphere, this change in relative rates is in the direction consistent with a significant inner-sphere contribution to the initial step in the reduction by Fe(II).

The preparation of water-soluble chelates of chromium(V) was described in 1979.[2] For several years we have been interested in redox reactions involving this unusual oxidation state. Earlier studies indicated that reductions of the bis chelate I with hydrazine[3] and with hydroxylamine,[4] as well as the disproportionation of Cr(V) as catalyzed by Ce(III),[5] entail preliminary loss of a



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(1) (a) Sponsorship of this work by the National Science Foundation (Grant 8313253) is gratefully acknowledged. (b) Present address: Chemistry Department, Pittsburgh State University, Pittsburgh, KS 66762.

(2) Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.

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Table I. Stoichiometry of the Cr^V–Fe^{II} Reaction[a]

mol of Fe^{II} taken ($\times 10^3$)	mol of Cr^V taken ($\times 10^4$)	mol of Fe^{III} formed ($\times 10^4$)[b]	$\Delta[Fe^{III}]/\Delta[Cr^V]$
1.05	2.10	4.25	2.02
1.32	2.63	5.00	1.90
1.67	3.33	7.00	2.10
1.85	3.70	7.38	1.99

[a] Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). Reactions were carried out in 0.05 M solutions of the parent hydroxy acid at pH 1. [b] Determined iodometrically.[8]

hydroxycarboxylato substituent but that the ligand environment about Cr(V) appears to be conserved in the reaction of Cr(V) with Ti(III).[6] Both the Ce(III)-catalyzed disproportionation and the reduction by Ti(III) may be taken to proceed through chromium(IV), but in neither instance has this intermediate been detected. The present report deals with the reduction of Cr(V) chelate I with Fe(II). Undoubtedly the most novel facet of this work is the appearance of a transient, the properties of which correspond to a complex of Cr(IV). This is, to our knowledge, the first instance in which this oxidation state has been observed in aqueous solution.

Experimental Section

Materials. Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (complex I) was prepared as its monohydrate as described by Krumpolc[2] and was kept in the dark at 0 °C; ϵ_{510} 165 M^{-1} cm^{-1} (lit.[2] 168 M^{-1} cm^{-1}).[7] Solutions of iron(II) perchlorate, prepared from the salt supplied by Alfa Chemicals, were standardized by titration with $Cr_2O_7^{2-}$.[8] Cation-exchange resin (Bio-Rad 50W-X2; 200–400 mesh), used in separation of reaction products, was pretreated as described.[9a] Lithium perchlorate, used in kinetic experiments, was prepared by the method of Dockal[9b] and recrystallized twice. 2-Ethyl-2-hydroxybutyric acid (Aldrich) was used as received.

Stoichiometric Studies. The redox reaction between Cr(V) complex I and Fe(II) was carried out in 0.05 M 2-ethyl-2-hydroxybutyric acid at pH 1.0 with Fe(II) taken in excess. The Fe(III) thus formed was determined iodometrically.[8] Titration data, summarized in Table I, indicate that very nearly 2.0 mol of Fe(III) is formed for every 1 mol of Cr(V) taken, provided that the reductant is in excess.[10] The resulting solutions gave negative tests for CrO_4^{2-}.

Examination of the Chromium(III) Reaction Products. A reaction mixture that was 0.0045 M in the Cr(V) complex (I), 0.0090 M in $Fe(ClO_4)_2$, and 0.050 M in the ligand acid (2-ethyl-2-hydroxybutyric acid) at pH 1.0 exhibited, after mixing, an absorption band at 585 nm (ϵ = 48 M^{-1} cm^{-1}) and a shoulder at 410 nm on the intense carboxylato–Fe^{III} absorbance in the UV.[11] When this mixture was subjected to cation-exchange chromatography at 2 °C,[12] a green eluate passed through the column quickly. The eluate exhibited maxima at 587 (ϵ = 50 M^{-1} cm^{-1}) and 415 nm (ϵ = 61 M^{-1} cm^{-1}) and constituted 57% of the total chromium taken. These peaks shifted when the mixture was allowed to stand for 8 h at pH 2 to 570 (ϵ = 24 M^{-1} cm^{-1}) and 412 nm (ϵ = 33 M^{-1} cm^{-1}). The trailing pale green band, containing the remainder of the dissolved chromium, was rapidly eluted with 0.5 M $HClO_4$ and exhibited peaks at 580 (ϵ = 38 M^{-1} cm^{-1}) and 413 nm (ϵ = 54 M^{-1} cm^{-1}). These slowly shifted to 570 (ϵ = 25 M^{-1} cm^{-1}) and 412 nm (ϵ = 33 M^{-1} cm^{-1}). Further changes in the spectrum were not observed after 10 h.

Rate Measurements. Reactions were monitored at 510 nm by using a Durrum-Gibson stopped-flow spectrophotometer. Total ionic strength was maintained at 0.50 M by addition of $LiClO_4$. When Fe(II) was taken in excess, a marked increase in absorbance, followed by a steep decrease, was observed. Depending on reagent concentrations, peak absorbances occurred 15–100 ms after mixing. With Fe(II) in larger excess, rate constants were evaluated by treating the kinetic profiles as consective first-order processes according to sequence shown in eq 1.

$$\text{Cr(V)} + \underset{\text{A}}{\text{Fe(II)}} \xrightarrow{k_0} \underset{\text{I}}{\text{intermediate}} \xrightarrow{k_1} \underset{\text{C}}{\text{products}} \qquad (1)$$

Since Fe(II) absorbs negligibly at 510 nm, absorbance–time profiles may be described by eq 2,[13,14] where D and D_∞ are the absorbances at time

$$D = A_0\epsilon_A e^{-k_0t} + \frac{\epsilon_I A_0 k_0}{k_1 - k_0}(e^{-k_0t} - e^{-k_1t}) + \frac{D_\infty}{k_1 - k_0}(k_0e^{-k_1t} - k_1e^{-k_0t}) + D_\infty \qquad (2)$$

t and at infinite time, ϵ_A and ϵ_I are the extinction coefficients of Cr(V) and the intermediate, and A_0 is the original concentration of Cr(V). The two pseudo-first-order rate constants, k_0 and k_1, were evaluated by using an iterative nonlinear least-squares refinement.[15,16] Calculated absorbances, from the final adjusted parameters, k_0, k_1, and ϵ_I, were in close agreement with observed absorbances, and deviations were randomly scattered for each run.

When the reaction was carried out with Cr(V) in large excess, an exponential growth of the intermediate was observed. Since this intermediate decayed only slowly,[17] the steps were kinetically separable, and rate constants for its growth were obtained from the usual logarithmic plots of absorbance differences vs. reaction times. Such plots were linear for more than 4 half-life periods. Rate constants generally agreed to better than 5% for runs with different master solutions.

Results and Discussion

From the determinations and stoichiometry (Table I) we see that with Fe(II) in excess, the net reaction may be represented schematically as (4).

$$Cr^V + 2Fe^{II} \rightarrow Cr^{III} + 2Fe^{III} \qquad (4)$$

As is the case with the reactions of Cr(V) with Ti(III),[6] Eu(II),[18] and VO^{2+},[18] the relatively high molar absorbances (ϵ_{587} =

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(3) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176.

(4) Rajasekar, N.; Subramaniam, R.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 971.

(5) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.

(6) Bose, R. N.; Gould, E. S. *Inorg. Chem.*, in press.

(7) Aqueous solutions of Cr(V) chelate I, if stabilized by 0.05 M 2-ethyl-2-hydroxybutyric acid at pH 3, decompose only slowly in the dark (less than 20% decomposition in 5 days at 25 °C). Such solutions, however, were found to undergo rapid decomposition to Cr(III) species in direct sunlight.

(8) Welcher, F. J. "Standard Methods of Chemical Analysis"; D. Van Nostrand: London, 1963; Part B, pp 688 and 750.

(9) (a) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792. (b) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *Ibid.* **1971**, *93*, 5661.

(10) Reactions of Fe(II) with excess Cr(V) in the presence of excess 2-ethyl-2-hydroxybutyric acid are complicated by disproportionation of a portion of the Cr(V) to Cr(III) and CrO_4^{2-}, a reaction that appears to be catalyzed by Fe(III). Attempts to determine Fe(III) spectrophotometrically as $Fe(NCS)^{2+}$ in our systems by addition of excess SCN^- were not successful due to competitive ligation of Fe(III) by the added hydroxy acid.

(11) The Fe^{III} complex of the anion of the parent hydroxy acid exhibits λ_{max} 350 nm, ϵ = 1.8 × 10^3 M^{-1} cm^{-1}.

(12) Separations were carried out by using Bio-Rad 50W-X2 sulfonate resin, H^+ form, 200–400 mesh, column length 5 cm, column capacity 2.0 mequiv. Use of a larger column led to more serious decomposition of the eluted Cr(III) complexes. For estimation of extinction coefficients of Cr(III) species, aliquots of each eluted fraction were oxidized with basic H_2O_2 and the total chromium content was determined as CrO_4^{2-}. See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand., Sect. A* **1952**, *48*, 414.

(13) See, for example: Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; Chapters 4 and 9.

(14) (a) Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, MA, 1974; pp 20–24. (b) Bose, R. N.; Viola, R. E.; Cornelius, R. D. *J. Am. Chem. Soc.* **1984**, *104*, 3336.

(15) A nonlinear least-squares program (written in Basic for the Apple II computer) was kindly provided by Professor J. H. Espenson and was used with minor modification. Trial values for the two rate constants were obtained graphically from biphasic plots,[14a] that for ϵ_I was obtained from experiments with Cr(V) in excess, and the parameters A_0, ϵ_A, and D_∞ were held invariant. Individual data points were unweighted.

(16) In a few instances, values of k_1 and k_0 were very nearly the same and refinement according to eq 2 did not converge. In these cases, kinetic profiles were analyzed according to eq 3 in which the parameters have

$$D = A_0\epsilon_A e^{-k_0t} + \epsilon_I k_0 A_0 t e^{-k_0t} - D_\infty e^{-k_0t}(1 + k_0t) + D_\infty \qquad (3)$$

the same meanings as those in eq 2.

(17) The slow decomposition of this intermediate (to a mixture of CrO_4^{2-} and one or more Cr(III) species) appears to be inhibited by H^+ and by the parent carboxylate ligand. A more detailed examination of this reaction is being carried out.

(18) Fanchiang, Y.-T.; Bose, R. N., unpublished experiments, Kent State University, 1984.

Table II. Representative Kinetic Data for Formation and Consumption of the Strongly Absorbing Intermediate[a] in the Reduction of (Carboxylato)chromium(V) with Iron(II) (21 °C, μ = 0.50 M)

10^3[Cr(V)],[b] M	10^3[Fe(II)], M	10^3[H$^+$],[c] M	[Lig$^-$],[d] M	$(k_f)_{obsd}$[e]	$(k_f)_{calcd}$[f]	k_c[g]
0.22	2.00	10.0	1.2	3.8	3.5	2.6
2.50	0.20	10.0	1.2	4.2	3.5	
0.11	1.00	10.0	2.4	6.9	6.4	2.4
0.30	3.00	10.0	2.4	5.9	6.4	2.5
2.02	0.20	10.0	2.4	7.2	6.4	
0.30	2.50	10.0	2.4	6.0	6.4	2.2
0.22	4.00	10.0	2.4	6.3	6.4	2.4
0.22	2.00	10.0	3.6	8.1	9.4	3.2
2.50	0.20	10.0	3.6	7.9	9.4	
0.22	2.00	10.0	4.8	10.1	12.3	3.4
2.02	0.20	10.0	4.8	10.4	12.3	
0.22	2.00	3.2	6.8	15.6	18.6	2.9
0.31	3.00	1.58	10.0	28	27	2.9
0.22	2.00	1.58	13.0	33	33	3.3
2.10	0.20	1.58	15.0	47	39	
2.40	0.20	1.58	25.0	62	63	
0.31	3.00	0.50	5.0	22	23	2.2
2.10	0.20	0.50	5.0	25	23	
2.00	0.20	0.50	10.0	35	35	
2.05	0.20	0.50	12.5	38	42	

[a] The extinction coefficient of this intermediate, which is proposed to be a Cr(IV) complex, (see text), is estimated as (13 ± 2) × 10^2 M^{-1} cm^{-1} at 510 nm from least-squares refinement of eq 2 and 3. [b] Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). [c] Estimated from the concentrations of ligand acid and its salt, taking K_A as 5.0 × 10^{-4} M.[3] [d] 2-Ethyl-2-hydroxybutyrate. [e] Second-order specific rates (in M^{-1} s^{-1} × 10^{-3}) for formation of the intermediate, estimated from analyses of biphasic kinetic curves as $k_0/[Fe^{II}]$(eq 2) when Fe(II) is in excess and from monophasic curves as $k_0/[Cr^V]$ when Cr(V) is in excess. [f] Second-order specific rates (in M^{-1} s^{-1} × 10^{-3}), estimated from rate law 5, taking k_{-H} as 5.3 s^{-1} and k_{Lig} as 2.46 × 10^6 M^{-2} s^{-1}. [g] Second-order specific rates (in M^{-1} s^{-1} × 10^{-4}) for consumption of the intermediate, estimated from analysis of biphasic kinetic curves as $k_1/[Fe^{II}]$ (eq 2) when Fe(II) is in excess.

50, ϵ_{415} = 61 M^{-1} cm^{-1})[19,20] and the ease with which the chromium(III) product is eluted from a cation-exchange column indicate that the primary reaction in this system yields predominantly, if not exclusively,[21] a unipositive bis-chelated complex of $(H_2O)_2Cr^{III}$. Slow decomposition of this product in solution and more rapid decay in contact with polysulfonic acid resin bring to mind analogous behavior already noted for (carboxylato)chromium(III) derivatives.[20c,22]

Since Fe(II) is ordinarily[23] taken to be a one-electron reductant, the intervention of tetrapositive chromium is to be expected. Reductions of Cr(V) by Ti(III)[6] and Eu(II)[18] should likewise pass through this oxidation state, but such an intermediate has not yet been detected in the latter two reactions. In the systems at hand, however, a strongly absorbing transient species (λ_{max} 515 nm, ϵ = 1.5 × 10^3 M^{-1} cm^{-1})[24] is observed. With Fe(II) in excess, the growth of this intermediate and its rapid reduction by Fe(II) may be monitored, whereas with Cr(V) in excess, exponential curves reflecting its growth are obtained, after which very slow disproportionation is apparent. The manner in which this intermediate is formed, the ease with which it is consumed by 1-e reductants in excess, and its perceived disproportionation[17] to Cr(III) and CrO_4^{2-} indicate it to be a Cr(IV) species. The observations that the same complex intervenes in the VO^{2+}–Cr(V) reaction and that it is ESR silent[25] at room temperature (suggesting the presence of an even number of d electrons)[26] support this assignment.

Kinetic data are summarized in Table II. Experiments with Fe(II) in excess generate biphasic kinetic curves that may be analyzed as a superposition of two consecutive pseudo-first-order processes.[13] One of these components reflects the growth of the intermediate, the other its disappearance. Both are found to be first order in Fe(II). The usual ambiguity associated with assignment of rate constants to such components[13] does not apply here, for the specific rate of growth may be independently evaluated under conditions where consumption is negligible.[27a] The consumption of the intermediate by excess Fe(II) proceeds at a specific rate (2.7 ± 0.4) × 10^4 M^{-1} s^{-1} (21 °C, μ = 0.50 M) and appears to be independent of acidity and ligand concentration in the range examined. The formation, designated k_f, may be described by eq 5. Values of specific rates for the inverse-[acid]

$$k_f = k_{-H}[H^+]^{-1} + k_{Lig}[Lig^-] \qquad (5)$$

term (k_{-H}) and the [ligand]-proportional term (k_{Lig}), obtained by nonlinear least-squares refinement[27b] of k_f values, are (5.3 ± 1.0) s^{-1} and (24.6 ± 1.2) × 10^5 M^{-2} s^{-1} (21 °C, μ = 0.50 M).

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(19) Nonchelated carboxylato complexes of $(H_2O)_5Cr^{III}$ and dicarboxylate complexes of $(H_2O)_4Cr^{III}$ exhibit ϵ values of 20–30, whereas chelated monocarboxylate complexes of $(H_2O)_4Cr^{III}$ are characterized by molar absorptivities between 30 and 40 M^{-1} cm^{-1}.[20]

(20) For comparisons of spectra of chelated and nonchelated carboxylate derivatives of Cr(III) see, for example: (a) Schlafer, H. L. *Z. Phys. Chem. (Wiesbaden)* **1957**, *11* 65. (b) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318. (c) Butler, R. D.; Taube, H. *Ibid.* **1965**, *87*, 5597; (d) Ward, J. R.; Haim, A. *Ibid.* **1970**, *92*, 475.

(21) The slight shift in absorbance maximum from 585 (ϵ = 48 M^{-1} cm^{-1}) to 587 nm (ϵ = 50 M^{-1} cm^{-1}) when the Cr(III) product is subjected to cation-exchange chromatography suggests the formation of a small quantity of a less strongly absorbing product, along with the predominant bis chelate, in the initial redox reaction.

(22) See, for example: (a) Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740 (footnote 10). (b) Hollaway, W. F.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 2181.

(23) There are a few instances in which conversion of Fe(II) to a transient Fe(IV) species have been proposed, but these generally involve systems featuring unusual chelating groups or particularly strong oxidants. See, for example: Levason, W.; McAuliffe, C. A. *Coord. Chem. Rev.* **1974**, *12*, 151. Kremer, M. L. *Trans. Faraday Soc.* **1963**, *59*, 2537. Cahill, A. E.; Taube, H. *J. Am. Chem. Soc.* **1952**, *74*, 3212. Groves, J. T.; Quinn, R.; McMurry, T. J.; Lang, G.; Boso, B. *J. Chem. Soc., Chem. Commun.* **1984**, 1455.

(24) This intermediate appears to persist only in the presence of excess Cr(V), which absorbs strongly in the ultraviolet.[2] Reflecting this constraint, useful UV spectra of the intermediate could not be obtained, even by difference.

(25) For example, when 1.0 mmol of the Cr(V) dichelate I is treated with 0.25 mmol of $VO(ClO_4)_2$ in the presence of excess parent hydroxy acid, the eight-line ESR spectrum characterizing VO^{2+} disappears, the single-peak associated with Cr(V) is reduced in magnitude by 24%, but no new resonances attributable to Cr(IV) are detected at room temperature (Gelerinter, E.; Fanchiang, Y.-T.; Bose, R. N., unpublished experiments, Kent State University, 1984).

(26) See, for example: Drago, R. S. "Physical Methods in Chemistry"; W. B.; Saunders Co.: Philadelphia, PA, 1977; Chapter 13.

(27) (a) Moreover, if assignment of rate constants to the two components were reversed, calculation of the maximum degree of conversion to the intermediate,[13] and thence its apparent extinction coefficient, yielded the value 5 × 10^2 M^{-1} cm^{-1} at 510 nm, in obvious disagreement with the value obtained with Cr(V) in excess. (b) In this refinement, which minimized the function $[(k_f)_{obsd} - (k_f)_{calcd}]^2$, individual data points were unweighted. Values of [H$^+$] were calculated from the concentrations of ligand carboxylic acid and its salt, taking K_A for the acid[3] as 5.0 × 10^{-4} M.

Table II also compares observed rates with those calculated by using (5).

Rate law 5 indicates the operation of two kinetic paths for the formation of the intermediate. Both activated complexes contain Fe(II) and Cr(V), but the k_{-H} path entails a loss of a proton, whereas the k_{Lig} path involves incorporation of an additional unit of ligand anion. The inverse-[acid] term may in principle arise either from reaction of $FeOH^+$ with the Cr(V) dichelate or form reaction of Fe^{2+} with the conjugate base of I. Since reduction by $FeOH^+$ requires a bimolecular rate constant near 3×10^{10} M^{-1} s^{-1}, which is comparable to the diffusion-controlled limit in aqueous media,[28,29] we conclude that the k_{-H} term stems principally from deprotonation of the hydrated form of the oxidant (which is thought to predominate in aqueous solution).[2] The k_{Lig} term in (5) is taken to reflect reduction of the dichelate by the complex $FeLig^+$; rate enhancement by carboxylato ligation of the reductant appears to be analogous to that observed in Cr(V)–Ti(III) systems.[6] Because acceleration is very nearly proportional to [Lig], the data at hand do not allow an estimate of the association constant for this complex or the specific rate at which it is oxidized.

Note that the Cr(V)–Fe(II) reaction differs from reduction of carboxylato-bound Cr(V) by hydrazine,[3] by hydroxylamine,[4] and from the Ce(III)-catalyzed disproportionation of Cr(V).[5] The last three reactions are strongly retarded by the parent ligand, implying a preliminary equilibrium in which a unit of ligand is lost from the oxidant prior to formation of a precursor complex with the reductant. These steps are required neither for the reaction at hand nor for its Cr(V)–Ti(III) counterpart.[6] In some instances, rates with Ti(III) appeared to exceed the rate of substitution at the reducing center, leading to assignment of an outer-sphere mechanism for the redox process. The recognized rapidity of substitution at Fe(II)[30] precludes our drawing a similar inference in the present system. Since our kinetic data suggest only a single path for disappearance of the strongly absorbing transient, we suspect that the two routes for its formation lead to a single species.

Although we can find no previous instance in which an intermediate having properties corresponding to Cr(IV) has been observed in aqueous solution, this oxidation state has been reported in mixed halide[31] and oxide[32] crystalline systems and in a series of molecular alkoxides.[33] Moreover, there is considerable indirect evidence for its intervention in a number of reductions of Cr(VI).[34] Since the observed extinction coefficient (1500 M^{-1} cm^{-1} at 515 nm) is probably much too large to reflect a d–d transition in an octahedral field, it is reasonable to suppose that we are dealing with a complex that features a noncentrosymmetric environment (i.e., tetrahedral or square pyramidal).

As in Ti(III)–Cr(V) reactions,[6] the primary Cr(III) product, which is taken to be a dichelate, is not thermodynamically favored, for it suffers slow aquation in the reaction medium employed. It is likely, but not certain, that its structure is related to that of the Cr(V) chelate taken, with the carboxyl functions trans to each other, the alcohol functions trans, and two coordinated H_2O groups also trans. The implication is then that the ligand connectivity has been preserved in both steps of the electron-transfer sequence ($Cr^V \rightarrow Cr^{IV}$ and $Cr^{IV} \rightarrow Cr^{III}$), and if this be the case, the Cr^{IV} intermediate may be taken to be a bis chelate, with, possibly, an additional (oxo, hydroxo, or aquo) ligand.[35,36]

Our inability to detect a Cr^{IV} intermediate in the reduction of Cr^V with Ti^{III} led to the suggestion[6] that the specific rate for reduction of such an intermediate with Ti^{III} was considerably greater than that for its generation. The minimum ratio of rates for these two processes, both of which were taken to be outer sphere, was estimated as 20. In the Fe(II)–Cr(V) system, the corresponding rates are found to be more nearly comparable, with that for the generation of the intermediate exceeding that for its consumption at high values of [Lig^-] (Table II), whereas the Marcus model for outer-sphere reactions[37] stipulates that this ratio should be very nearly independent of the reductant. Although differences in the detailed rate laws associated with the two reductants complicate comparisons, the inversion in relative rates is in the direction consistent with a significant inner-sphere contribution to the initial step in the reduction by Fe(II).[38] No such conclusion is possible for reduction of the intermediate.[39]

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Appendix

Derivation of Eq 3. Consider a reaction sequence

$$A + B \xrightarrow{k} I \xrightarrow{k} C \tag{a}$$

with I an intermediate and the two rate constants (k) the same. Under pseudo-first-order conditions, with B in excess, and with the absorbance of B negligible at the wavelength at hand, we may represent the total absorbance D_t at time t as

$$D_t = \epsilon_A[A] + \epsilon_I[I] + \epsilon_C[C] \tag{b}$$

where ϵ values represent extinction coefficients of the species indicated. Reactant A suffers an exponential loss, (c), whereas the concentration of intermediate I has been shown to follow (d)[13]

$$[A] = A_0e^{-kt} \tag{c}$$

$$[I] = kA_0te^{-kt} \tag{d}$$

Mass balance implies

$$[C] = A_0 - [A] - [I] \tag{e}$$

Substitution of (c), (d), and (e) into (b) yields

$$D_t = \epsilon_A A_0e^{-kt} + \epsilon_I kA_0te^{-kt} + \epsilon_c(A_0 - [A] - [I]) \tag{f}$$

Removal of the final parentheses and substitution of (d) yield

$$D_t = \epsilon_A A_0e^{-kt} + \epsilon_1 kA_0te^{-kt} + \epsilon_C A_0 - \epsilon_C A_0e^{-kt} - \epsilon_C kA_0e^{-kt} \tag{g}$$

D_0, the initial absorbance, is $\epsilon_A A_0$, whereas D_∞, the final absorbance, is $\epsilon_C A_0$. Substitution into (g) and then rearranging terms yield

$$D_t = D_0e^{-kt} + \epsilon_I kA_0te^{-kt} - D_\infty e^{-kt}(1 + kt) + D^\infty \tag{3}$$

which is given in a slightly different version in ref 16.

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(28) The value 3×10^{10} M^{-1} s^{-1} is obtained by dividing k_{-H} by the recorded[29] acidity constant, 2×10^{-10} M, for Fe^{2+}(aq). The diffusion-controlled limit for reactions of this type in solution lies near 2×10^{10} M at 25 °C.[13]

(29) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1976; Vol. 4, p 5.

(30) See, for example: Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1968; p 155.

(31) Clark, H. C.; Sandana, Y. N. *Can. J. Chem.* **1964**, *42*, 50.

(32) Wilhelmi, K.; Jonson, O. *Acta Chem. Scand.* **1961**, *15*, 1415.

(33) (a) Hagihara, M.; Yamasaki, H. *J. Am. Chem. Soc.* **1959**, *81*, 3160. (b) Alyea, E. C.; Basi, J. S.; Bradley, D. C.; Chisholm, M. H. *J. Chem. Soc. A*, **1971**, 772. Note that these authors report Cr(IV) to be ESR silent at temperatures above 98 K.

(34) See, for example: (a) Tong, J. Y.; King, E. L. *J. Am. Chem. Soc.* **1960**, *82*, 3805. (b) Espenson, J. H. *Ibid.* **1964**, *86*, 5101. (c) Rahman, M.; Roček, J. *Ibid.* **1971**, *93*, 5455, 5462. (d) Roček, J.; Peng, T. Y. *Ibid.* **1977**, *99*, 7622.

(35) If our assignment of a bis-chelated structure to the principal Cr(III) product is correrct, it follows that, as is the case with Ti(III),[6] reduction of Cr(IV) proceeds more rapidly than ligand substitution at that metal ion center in our systems. Indirect evidence[36] suggests that this is not the case when Cr(IV) is consumed by the less powerful reductants, Mn(II) and Ce(III).

(36) See, for example: (a) Ogard, A. E.; Taube, H. *J. Phys. Chem.* **1957**, *62*, 357. (b) Plane, R. A.; Taube, H. *Ibid.* **1952**, *56*, 33.

(37) (a) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(38) See, for example: Gould, E. S. *Inorg. Chem.* **1979**, *18*, 900.

(39) Two comments by a reviewer deserve response. First, he expressed surprise at our earlier suggestion[6] that the reduction of Cr(V) by $TiOH^{2+}$ is principally an outer-sphere process in view of the known propensity of Ti(III) for oxygen donors. It appears here that high outer-sphere rates reflect the very favorable $\Delta E°$ associated with the Cr(V)–Ti(III) reaction, whereas the importance of the inner-sphere route is limited by the relatively slow substitution at the Ti(III) center. In addition, the reviewer asked why a k_{Lig} term is not observed for the reduction of the Cr(IV) intermediate as well as for its formation. On the latter point we remain puzzled.