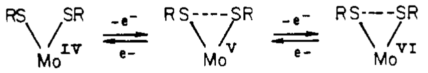
transfer process. It is possible that the cis positioning of molybdenum-bound thiolates brings these reactivity changes to molybdenum sites in enzymes, such that a triatomic unit may be responsible for some of the unique spectroscopic and reactivity parameters of these sites.



The static distortions of the Mo(VI) coordination sphere observed in these studies have potential impact on structural and mechanistic considerations for the molybdenum sites in enzymes. Heretofore, all suggestions for the structure of the molybdenum site have been based on octahedral geometries. However, the results of our studies clearly show that relatively small, but sterically demanding, changes in the ligands can lead to severe distortions in the molybdenum coordination sphere. Certainly, a set of donor ligands from a protein or cofactor could be equally demanding and, in attempting to model the molybdenum site, we must take account of this deformability in our choice or design of ligand systems.

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Registry No. **1**, 74005-67-7; **2**, 76772-96-8; **3**, 74005-68-8.

Supplementary Material Available: Listings of anisotropic thermal parameters, calculated hydrogen atom positions, and observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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Reduction of Perchlorate Ion by (*N*-(Hydroxyethyl)ethylenediaminetriacetato)aquotitanium(III)

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In acidic, aqueous chloride media (LiCl, 2 M) at 25 °C, reduction of perchlorate ion by (*N*-(hydroxyethyl)ethylenediaminetriacetato)aquotitanium(III) (Ti(Hedta)) follows the rate law rate = $(k[\mathrm{ClO_4^-}][\mathrm{H^+}]^2 + k')[\mathrm{Ti(Hedta)}]$, where $k = 2 \times 10^{-3}$ M^{-3} s^{-1} and $k' = 2 \times 10^{-8}$ s^{-1}. The acid dependence is consistent with an inner-sphere mechanism with rate-determining distortion of protonated perchlorate. Such distortion leads to increased interaction between an electron-donor orbital centered on titanium and an electron-acceptor orbital centered on chlorine.

In acidic aqueous solutions, $\mathrm{Cr^{2+}}$ shows no reaction with perchlorate ion, but $\mathrm{Ti^{3+}}$ (thermodynamically a weaker reductant) does react at a measurable rate.[1] Two explanations have been proposed for this anomaly. Kallen and Earley[2] concluded that the rate-determining factor is interaction of polarizable d orbitals of the metal ion with a chlorine-centered orbital. Taube[3] proposed an alternative rationalization, that the relative stability of the –yl product is dominant. ($\mathrm{TiO^{2+}}$, titanyl ion, is well-known, but there is no corresponding chromium species.) We now report results of experiments designed to distinguish between these two plausible explanations.

The stoichiometry of the reaction between (*N*-(hydroxyethyl)ethylenediaminetriacetato)aquotitanium(III)[4] (hereafter, Ti(Hedta)) and $\mathrm{ClO_4^-}$ was determined spectrophotometrically to be

$$8\mathrm{Ti^{3+}} + \mathrm{ClO_4^-} + 8\mathrm{H^+} \rightarrow 8\mathrm{Ti(IV)} + 4\mathrm{H_2O} + \mathrm{Cl^-}$$

Kinetics were studied at 25 °C by measuring the decrease in absorbance at 550 nm, due to Ti(Hedta). Procedures were generally as previously described.[4] Preequilibrated Ti(Hedta) was injected to start the reaction. Kinetic runs followed first-order kinetics for at least 2 half-times (perchlorate was in large excess). In some experiments, there was a small initial increase in absorbance during times up to 50 min. This effect was not present if mixing was complete. There was a slow increase in absorbance at long times, assignable to polymerization of Ti(IV). Rate constants were calculated by linear least squares. Kinetic data are shown in Table I.

Increasing [Hedta] to values higher than the stoichiometric amount does not affect the rate of the reaction at constant acidity. Change of medium from hydrochloric acid to trifluoromethanesulfonic acid (hereafter, HTFMS) has small effect, but the reaction is definitely slower in less concentrated salt media. At constant acidity, the observed first-order rate constant increases linearly as $\mathrm{ClO_4^-}$ concentration increases. At constant [Ti(Hedta)] and $[\mathrm{ClO_4^-}]$, rate increases as $[\mathrm{H^+}]$ increases, but acid catalysis is not linear. The data at high acidity are best fitted by second-order dependence on $[\mathrm{H^+}]$. At low acidity and/or low perchlorate concentration, the observed rate is somewhat higher than that to be expected on the basis of a one-term rate law. This is taken into account here by a second, constant term. Ti(Hedta) is somewhat more stable than $\mathrm{Ti^{3+}}$, insofar as air oxidation is concerned, but some loss of Ti(III) occurred over the (several days!) course of these reactions. Any perchlorate reduction through acid-independent and linearly acid-dependent terms are also included in this small correction. Our data are adequately fitted by the rate law

$$\text{rate} = (k[\mathrm{ClO_4^-}][\mathrm{H^+}]^2 + k')[\mathrm{Ti(Hedta)}]$$

where $k = 2 \times 10^{-3}$ M^{-3} s^{-1} and $k' = 2 \times 10^{-8}$ s^{-1} at 25 °C in 2 M lithium chloride medium.

In the case of the reduction of perchlorate ion by $\mathrm{Ru^{2+}}$, there is convincing evidence that the overall rate of the redox reaction

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[1] Duke E. R.; Quinney P. R. *J. Am. Chem. Soc.* **1954**, *76*, 3800.
[2] Kallen, T. W.; Earley, J. E. *Inorg. Chem.* **1971**, *10*, 1152.
[3] Taube, H. *ACS Symp. Ser.* **1982**, *No. 198*.
[4] Lee, R. A.; Earley, J. E. *Inorg. Chem.* **1981**, *20*, 1739.

Table I. Kinetics of Reduction of Perchlorate Ion by Ti(Hedta) at 25.0 °C in 2.0 M LiCl

[Ti(III)]/ mM	$[H^+]$/ cM	$[ClO_4^-]$/ cM	[Hedta]/ mM	k_{obsd}/ 10^{-7} s^{-1}	k_2[a]/ 10^{-6} M^{-1} s^{-1}	k_4[b]/ 10^{-4} M^{-3} s^{-1}
5	10	100	5	124	11	11
8	10	50	8	148	26	26
10	5	50	12	58	8	30
10	5	50	10	77	11	46[c,g]
10	10	5	10	32	24	24
10	10	25	10	76	22	22
10	10	50	0	580	111	
10	10	50	10	121	20	20
10	10	50	10	175	31	31[c,d]
10	10	50	12	60	8	8[c,e]
10	10	50	12	140	24	24
10	10	50	20	140	24	24
10	10	50	25	140	24	24
10	10	50	30	142	24	24
10	10	100	12	270	25	25
10	10	100	10	475	46	46[g,c]
10	10	100	10	267	25	25
10	12	50	12	102	16	11
10	12	50	12	123	20	14
10	12	50	12	190	34	24
10	12	50	12	117	19	13
10	13	50	10	513	99	58[c,g]
10	14	50	12	281	52	27
10	17	50	12	274	51	18
10	19	50	12	689	134	37
10	20	50	10	220	40	10
10	20	50	12	492	94	24
10	20	50	12	559	108	27
10	20	50	12	430	82	21[f,c]
10	22	50	12	420	80	17
10	22	50	12	377	71	15
10	24	50	12	580	112	19
10	24	50	12	600	116	20[f,c]
15	10	50	0	560	108	
15	10	100	12	139	12	12
15	13	50	0	640	124	
20	10	100	21	80	6	6[c,g]
20	20	50	24	256	47	12
20	20	50	30	253	47	12
30	20	50	34	255	47	12
40	20	50	50	114	18	5
40	20	50	80	175	31	8[c,g]
						18 ± 8 (av)[h]

[a] $(k_{obsd} - (2 \times 10^{-8}\ s^{-1}))/[ClO_4^-]$. [b] $k_2/[H^+]^2$. [c] Not included in average. [d] Ionic strength 3 M. [e] Ionic strength 1 M. [f] HTFMS medium, 1.5 M. [g] Deviation twice rms deviation. [h] Rms deviation.

is determined by the rate of the Ru(II) substitution reaction that leads to formation of a binuclear intermediate in an inner-sphere mechanism. The rate constant for reduction of 0.5 M perchlorate ion (0.1 M HCl–1.9 M LiCl) by Ti(Hedta) is about one-fourth as large as the corresponding rate constant for reduction of the same oxidant by Ti^{3+}. The rate constant for reaction[4] of $Ru(NH_3)_5NCS^{2+}$ by Ti^{3+} is 840 M^{-1} s^{-1}, and that for reduction of the same oxidant by Ti(Hedta) is 27.5×10^4 M^{-1} s^{-1}. Rates of these reactions are limited by substitution on Ti(III). The rates we observe are much slower than those that pertain to Ti(III) substitution reactions but much faster than those that pertain to replacement of oxygen from perchlorate ion or for outer-sphere electron transfer to perchlorate ion (neither of these processes is fast enough to be observed in any known system). The only plausible mechanism for the present reaction is an inner-sphere mechanism involving a Ti(III)–perchlorate complex. For both Ti(III) reductants, previously measured data indicate that formation of a Ti(III)–perchlorate complex would be a rapid equilibrium. This indicates that the rate-determining process involves electron transfer within that intermediate. The decrease in overall redox rate on complexation is best understood as corresponding to increased rate of dissociation, and hence reduced stability, of the intermediate perchlorate–Ti(III) complex, due to the lower positive positive charge of the Ti(III)–ligand complex, as compared with the uncomplexed Ti(III) reductants (Ti^{3+} and $TiOH^{2+}$).

Reduction of perchlorate ion by Ti^{3+} in dilute solution is reported to have both an $[H^+]$-dependent and also an $[H^+]$-independent path.[1] The rate of reduction of perchlorate ion by Ti(Hedta) is dependent on the square of the hydrogen ion concentration (0.050 M < $[H^+]$ < 0.24 M). Edwards[5] has shown that the reactions of oxyanions with bases often involve terms with second-order and higher order dependencies on acid concentration. This is interpreted as indicating that proton-assisted distortion of the anion is a necessary precondition for reaction.

Our data are consistent with the mechanism

$$\mathrm{Ti(Hedta)} + \mathrm{ClO_4^-} \xrightleftharpoons{\text{rapid}} \mathrm{Ti(Hedta)OClO_3^-} + \mathrm{H_2O}$$

$$\mathrm{Ti(Hedta)OClO_3^-} + 2\mathrm{H^+} \rightleftarrows \mathrm{(Hedta)TiOClO_3H_2^+}$$

$$\mathrm{(Hedta)TiOClO_3H_2^+} \xrightarrow{\text{slow}} [\mathrm{(Hedta)TiOClO \cdots (OH)_2}]^+$$

$$[\mathrm{(Hedta)TiOClO_2 \cdots (OH)_2}]^+ \xrightarrow{\text{rapid}} \text{products}$$

The rate-determining step involves distortion of an intermediate containing protonated oxygen. If two protons were

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(5) Edwards, J. O. *Chem. Rev.* **1951**, *50*, 455.

complexed to a single oxygen atom, the chlorine center would distort toward (but certainly not to) a trigonal geometry; in the more likely event of protonation of two oxygens, distortion (clearly not complete) in the direction of a square-planar geometry about chlorine would be expected. Either of these two types of distortion (even if fairly small) would lower the energy of the LUMO of the perchlorate[6] group (which would be expected to have the same symmetry with respect to a Ti–O–Cl axis as the electron-donor orbital of Ti). Once interaction of an electron-donor orbital (titanium t_{2g}) and an electron-acceptor orbital (involving chlorine p and/or d π orbitals) had been facilitated by distortion, electron transfer should be rapid. On this view, distortion of perchlorate to permit electronic overlap (the third step above) is rate determining.

In proposing the alternative mechanism, Taube suggested[3] that the acid dependence reported for the Ti^{3+}–perchlorate reaction might be an artifact, since no acid dependence would be expected on the basis of his hypothesis. The previously reported acid dependence for the Ti^{3+}–perchlorate reaction is consistent with the present results. Rates of redox reactions of Ti^{3+} are normally inversely proportional to $[H^+]$, because reaction goes through $Ti(OH)^{2+}$. If distortion of a doubly protonated intermediate were also operative in the Ti^{3+}–perchlorate reaction, the net result would be a term with a first-order dependence on acid, as reported. In the case of reduction of perchlorate ion by (*N*-(hydroxyethyl)ethylenediaminetriacetato)aquotitanium(III), the amino acid ligand prevents proton dissociation from Ti^{3+} and blocks the $TiOH^{2+}$ path, with the result that the acid dependence is large. Our present results are consistent with Kallen and Earley's rationalization of the bizarre rate order of cation reduction of perchlorate. The difficulty, noted by Taube, of reconciling an acid dependence with the alternate (–yl ion) rationalization indicates that the present results are not consistent with that alternate mechanism.

Acknowledgment. $LiCF_3SO_3$ and CF_3SO_3H solution were kindly supplied by Dr. Patrizia Barone. We are grateful for helpful discussion with Professors Karl Wieghardt and Miklos Kertesz and to Ke-jean Lu for experiments on the initial irregularity.

Registry No. Ti(Hedta), 77704-13-3; ClO_4^-, 14797-73-0.

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[6] Johansen, H. *Chem. Phys. Lett.* **1971**, *11*, 466.

Notes

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Reactions at the Metal Vertex of a Ruthenacarborane Cluster. Activation of Carbon Monoxide by *closo*-3,3,3-$(CO)_3$-3,1,2-$RuC_2B_9H_{11}$

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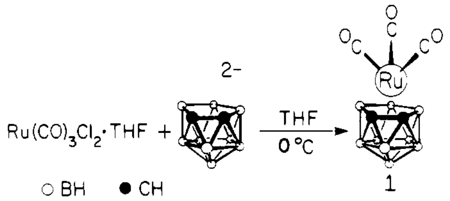
Received December 20, 1983

Activation of coordinated CO with respect to nucleophilic attack has been proposed to be an important aspect of the homogeneous catalysis of the water gas shift reaction as well as organic reductions employing CO/H_2O mixtures.[1] Furthermore, this mode of activation represents the primary route to transition-metal formyl complexes, proposed as intermediates in the conversion of CO/H_2 mixtures to oxygenated organic products.[2] In light of these observations, we have investigated the chemistry of *closo*-3,3,3-$(CO)_3$-3,1,2-$RuC_2B_9H_{11}$ (**1**), which we have found to be highly reactive toward nucleophiles. The results of this study and subsequent chemistry will provide the basis for this note.

Results and Discussion

The synthesis of **1** was first reported by Siedle[3] who reacted $[Ru(CO)_3Cl_2]_2$ with 7,8-$C_2B_9H_{11}^{2-}$ in refluxing THF to produce **1** in 7% yield. We have improved the yield to 65% by employing a slow addition of 7,8-$C_2B_9H_{11}^{2-}$ to a stirred THF solution of $Ru(CO)_3Cl_2{\cdot}THF$[4] at 0 °C (eq 1). In this way, exposure of the product **1** to the nucleophilic $C_2B_9H_{11}^{2-}$ dianion is minimized and the yield is optimized. The high terminal C≡O stretching frequencies of **1** (2090, 2030 cm^{-1}) suggests that these ligands should be reactive toward nucleophiles since reduced π^* back-bonding effectively decreases the electron density at the carbonyl carbon.[5] In fact, **1** was found to react rapidly with a range of nucleophiles, the results being summarized in Scheme I.



(1)

Addition of 1 molar equiv of $K^+B(sec\text{-}C_4H_9)_3H^-$ to an NMR tube containing a THF solution of **1** cooled to −78 °C resulted in the observation of a singlet in the ^1H FTNMR spectrum at δ 14.1, attributed to the anionic formyl complex **2** (Scheme I). Warming the NMR tube to 0 °C converts **2** to the anionic dicarbonyl hydride complex **3** with a time for half-reaction of ca. 30 min. This mode of decomposition of the formyl complex **2** is well established[2] although the stability of **2** differs markedly from that of the neutral analogue, $(C_5H_5)Ru(CO)_2CHO$, which decomposes rapidly at −90 °C.[6]

The complex **3** was also prepared by the reaction of **1** in THF with an excess of aqueous KOH (Scheme I). This reaction may be viewed as the decarboxylation of an intermediate hydroxy carbonyl adduct or metallocarboxylic acid **4**. Although this intermediate was not directly observed, reaction of **1** with methanolic KOH quantitatively produced the metallocarboxylic acid ester **5**. This complex was thermally stable but reacted rapidly with acid to regenerate **1** and methanol (Scheme I).

Compounds **3** and **5** have precedent with the analogous $(C_5H_5)Ru(CO)_2H$[7] and $(C_5H_5)Ru(CO)_2COOMe$[8] but differ

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[1] Gross, D. C.; Ford, P. C. *Inorg. Chem.* **1982**, *21*, 1704 and references therein.

[2] For a recent review see: Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

[3] Siedle, A. R. *J. Organomet. Chem.* **1975**, *90*, 249.

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[5] Angelici, R. J.; Blacik, L. J. *Inorg. Chem.* **1972**, *11*, 1754.

[6] Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43.

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