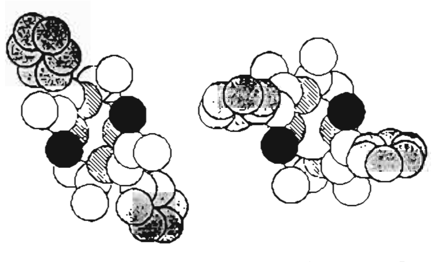

$[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$ $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$

Figure 4. View along the C_2 axes of space-filling representations of $[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$ and $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$. Data were taken from ref 4 and 5. Oxygen atoms are shown in black, nitrogen atoms are shown as striped, and the shaded areas indicate the positions of the phenyl rings of interest.

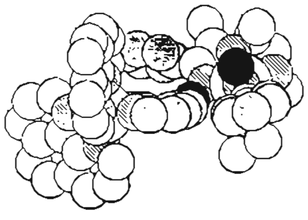

Figure 5. Possible stacking type interaction (shaded) between a 1,10-phenanthroline ring on $[\text{Co(phen)}_3]^{2+}$ and the phenyl rings on $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$. Additional data were taken from ref 38.

repulsion is unlikely to produce effects that are significant enough to explain the observed stereoselectivities. For example, the proportion of the rate carried by the C_2 axis face is 15.8% for $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$ and 13.9% for $[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$ but is 15.4% for $[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(2)}]^{2+}$, which shows stereoselectivity closer to that of $[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$ than that of $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$. Some modification of the model is required.

The reductant $[\text{Co(phen)}_3]^{2+}$ presents a hydrophobic aspect and will tend to associate predominantly with hydrophobic faces of the oxidant. For $[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(2)}]^{2+}$, this amounts to almost the whole ion apart from the hydrophilic C_2 face where the oxime oxygens are located. Addition of hydrophobic phenyl groups to the complex ion on the amine and oxime–imine framework away form this C_2 face will have little effect on the proportion of the reaction taking place through the hydrophilic face, and hence the stereoselectivities will be rather insensitive to these changes, as is observed with $[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$ and the dibenzyl derivative $[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(3)}]^{2+}$. For $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$, the phenyl groups straddle the hydrophilic C_2 face, increasing its hydrophobic character. Indeed, the two phenyl rings form a cleft that might support a stacking interaction as shown in Figure 5. An interaction of this sort in addition to electrostatic forces provides an explanation for the modest rate enhancement in the cross-reaction between $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$ and $[\text{Co(phen)}_3]^{2+}$. Thus, the stereoselectivity for $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$ can be explained by the placement of the hydrophobic phenyl groups along the normally hydrophilic C_2 axis of the oxidant and the proposal that reaction along this axis exhibits the opposite chirality from that predominating for the rest of the complex ion. A similar conclusion has been reached in the reduction by $[\text{Co(edta)}]^{2-}$.

The results strongly suggest that the modest stereoselectivities detected in outer-sphere electron-transfer reactions between metal ion complexes are the result of the multiplicity of orientations of the complexes which give acceptable orbital overlap for electron transfer rather than intrinsically small stereoselectivities for particular orientations. They further suggest that electron transfer in these systems has little intrinsic orientation requirements other than those imposed by the precursor structure.

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Registry No. $[\text{Co(phen)}_3]^{2+}$, 16788-34-4; $[\text{Ni}^{IV}\text{Me}_2\text{L(1)}]^{2+}$, 55188-33-5; $[\text{Ni}^{IV}\text{MePhL(1)}]^{2+}$, 55758-54-8; $[\text{Ni}^{IV}\text{PhMeL(1)}]^{2+}$, 55822-44-1; $[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(2)}]^{2+}$, 99342-18-4; $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$, 110077-01-5; $[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(3)}]^{2+}$, 110077-03-7; $[\text{Ni}^{IV}\text{Me}_2\text{L(4)}]^{2+}$, 114157-52-7; $[\text{Co(4,7-Me}_2\text{phen)}_3]^{2+}$, 47872-45-7; $[\text{Co(5,6-Me}_2\text{phen)}_3]^{2+}$, 47872-55-9; $[\text{Co(bpy)}_3]^{2+}$, 15878-95-2; $[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$, 110095-00-6.

Supplementary Material Available: Listings of pseudo-first-order rate constants for the oxidation of $[\text{Co(phen)}_3]^{2+}$ and its derivatives by nickel(IV) (Table SI), nickel(III) (Table SII), and $[\text{Co(terpy)}_2]^{3+}$ (Table SIII) (14 pages). Ordering information is given on any current masthead page.

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Electron Transfer. 93. Further Reactions of Transition-Metal-Center Oxidants with Vitamin B_{12s} (Cob(I)alamin)[1]

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Vitamin B_{12s} (cob(I)alamin) reduces europium(III), titanium(IV) ($\text{TiO(C}_2\text{O}_4)_2^{2-}$), and uranium(VI) in aqueous solution. These oxidants undergo one-electron changes, leading in each case to the cobalt product cob(II)alamin (B_{12r}). The reduction of Eu^{3+}, which is inhibited by "TES" buffer, but not by glycine, is outer sphere. Its limiting specific rate (1×10^2 M^{-1} s^{-1}), incorporated in the Marcus treatment, yields a B_{12s},B_{12r} self-exchange rate of $10^{4.8\pm0.5}$ M^{-1} s^{-1}. Reductions of $\text{TiO(C}_2\text{O}_4)_2^{2-}$ are accelerated by H^+ and by acetic acid. Kinetic patterns suggest three competing reaction paths involving varying degrees of protonation of the Ti(IV) center or its association with acetic acid. The very rapid reduction of U(VI) ($k = 4 \times 10^6$ M^{-1} s^{-1}) yields U(V) in several buffering media, even when B_{12s} is taken in excess. The much slower conversion of U(V) to U(IV), although thermodynamically favored, appears to be retarded by the extensive reorganization of the coordination sphere of oxo-bound U(V) that must accompany its acceptance of an additional electron. The observed specific rate for the B_{12s}–U(VI) reaction is in reasonable agreement, in the framework of the Marcus formalism, with reported values of the formal potential and the self-exchange rate for U(V,VI).

Vitamin B_{12s} (cob(I)alamin, the cobalt(I) analogue of B_{12a}) reacts rapidly and quantitatively with an imposing array of inorganic and organic oxidants.[2] Much of the early work with this macrocyclic reductant, which dealt with its role in organic syn-

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[1] Joint sponsorship of this work by the National Science Foundation and the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health (Grant No. BRSG S07 RR-07208-8) is gratefully acknowledged.

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Table I. Stoichiometry of the Reaction of Vitamin B_{12s} (Cob(I)alamin) with Uranium(VI)[a]

$10^5[U(VI)]$[b]	$10^5[B_{12s}]$	pH	$10^5\Delta[B_{12s}]$	$\Delta[B_{12s}]/\Delta[U(VI)]$
0.81	4.93	4.91[c]	0.92	1.13
1.62	4.58	4.92	1.88	1.15
2.40	5.13	4.92	2.53	1.10
3.18	5.83	4.95	3.79	1.19
6.12	9.37	4.90	7.06	1.15
2.54	5.63	2.71	2.73	1.08
3.35	5.93	2.52	3.58	1.07
4.14	7.60	2.39	4.74	1.14
4.92	8.40	2.53	5.55	1.13

[a] Reactions were monitored at 387 nm. Concentrations are given in molarity. [b] Added as $UO_2(ClO_4)_2$. [c] Solutions having pH 4.9–5.0 were buffered with acetic acid and acetate. Acidities of solutions with pH 2.4–2.7 were regulated by addition of dilute $HClO_4$.

thesis,[3] centered about conversions in which B_{12s} was, in effect, a 2-electron donor, and more recent mechanistic studies emphasized this mode of action.[4,5] In contrast, reactions of B_{12s} with the transition-metal centers cobalt(III),[6] vanadium(IV),[7] and molybdenum(VI)[7] involve single-electron transactions, with the latter two leading to autocatalytic sequences. Still other reagents, e.g., organic disulfides[8] and oxyhalogens,[9] oxidize B_{12s} cleanly, but whether one or two electrons are transferred in the initiation processes remains, in these instances, an open question.

The present report describes the reactions of B_{12s} in aqueous solution with ionic centers featuring the oxidation states europium(III), titanium(IV), and uranium(VI). Although the kinetic pictures associated with these oxidants are more straightforward than those with V(IV) and Mo(VI),[7] results with U(VI) were not altogether as expected.

Experimental Section

Materials. Potassium bis(oxalato)oxotitanate(IV) $K_2TiO(C_2O_4)_2\cdot 2H_2O$ (Alfa) was recrystallized from a minimum volume of water and dried to 110 °C before use. Sodium borohydride and glycine (Fisher) and hydroxocobalamin hydrochloride (Sigma) were used as received, as were the Aldrich buffers "TES" (2-[(tris(hydroxymethyl)methyl)amino]-1-ethanesulfonic acid) ($pK_A = 7.50$) and "MES" (4-morpholineethanesulfonic acid) ($pK_A = 6.15$). Solutions of the perchlorates of Eu(III) and U(VI) were prepared by dissolving Eu_2O_3 (99.9%) and UO_3 in $HClO_4$ and then partially neutralizing them with NaOH. Solutions of U(VI) were standardized spectrophotometrically.[10] Sodium perchlorate, for kinetic experiments, was prepared by treatment of $NaHCO_3$ with $HClO_4$. All reactions were carried out under oxygen-free N_2 in distilled water that had been previously boiled and sparged with N_2 for at least 4 h.

Cob(I)alamin was generated in solution from the cobalt(III) complex hydroxocobalamin hydrochloride by using zinc amalgam for reduction in acid solution[4] and $NaBH_4$–$PdCl_4^{2-}$ in basic solution.[5] Kinetic runs with Eu^{3+} or Ti(IV) at pH values below 4 were carried out with the amalgam in the reaction vessel,[4] but with U(VI), B_{12s} was generated in dilute $HClO_4$ and then transferred carefully by syringe to the buffered supporting medium just before adding the oxidant.

Stoichiometric Studies. The stoichiometry of the reaction of U(VI) with excess B_{12s} was determined by forming Co(I) in acid solution, buffering the solution if necessary, adding a known deficiency of $UO_2(ClO_4)_2$, waiting 5 min, and then measuring the decrease in absorbance at 387 nm. The resulting changes were compared with those occurring when B_{12s} was treated with excess oxidant. Corrections were made for the loss in absorbance (less than 10%) when the corresponding volume of dilute $NaClO_4$ was added to B_{12s}. Results are summarized in Table I.[11]

Kinetic Studies. Rates were estimated from measurements of decreases of absorbance at 387 nm. Reactions with Eu(III), Ti(IV), and Re(VII) were studied on a Beckman Model 5260 recording spectrophotometer, whereas the more rapid reductions of U(VI) were run on a Durrum-Gibson stopped-flow spectrophotometer. Acidities were regulated by addition of appropriate concentrations of buffering acids and their conjugate bases to the reductant before mixing; pH values of the resulting solutions were confirmed experimentally. Total ionic strength was maintained at 0.20 ± 0.02 M by addition of $NaClO_4$. Reagent concentrations were adjusted so that the slow decomposition of B_{12s} in aqueous medium was negligible in relation to the reactions of interest.

Reactions were first order each in B_{12s} and in oxidant but were generally carried out with the oxidant in greater than 10-fold excess. Conversions were followed for at least 5 half-lives. Specific rates from successive half-life values within a run generally agreed to within 5%, and average values did not differ significantly from those obtained from slopes of logarithmic plots of absorbance differences against reaction time. Specific rates from replicate runs diverged by less than 10%.

Oxidations of B_{12s} by a number of oxidants were too rapid to follow, even with stop-flow techniques. Among these were $IrCl_6^{2-}$, carboxylato chelates of $Cr^V(=O)$,[12] Fe^{III}_{aq}, $Fe^{III}EDTA$, Cu^{II}_{aq}, and $Ru(NH_3)_6^{3+}$. Bimolecular specific rates (25 °C) for each exceeded $5 \times 10^6\ M^{-1}\ s^{-1}$. Reactions with the first four of these oxidants (in excess) yielded B_{12a} (hydroxocob(III)alamin), whereas Cu(II) and $Ru(NH_3)_6^{3+}$ yielded cob(II)alamin. In contrast, reactions with Cr^{III}_{aq} and Yb^{III}_{aq} (if any) at pH 2.6–4.5 failed to compete with the decay of B_{12s} in the media; the estimated upper limit for these tripositive species is $0.08\ M^{-1}\ s^{-1}$. B_{12s} reacted with $NaReO_4$, $MoOCl_5^{2-}$,[13] $MoO_4(EDTA)^{2-}$,[14] and Sn(IV) (in HCl), but the first two of these yielded autocatalytic curves similar to those observed with MoO_4^{2-},[7] whereas the latter two oxidants gave biphasic profiles that could not be simply interpreted.

All reactions proceeding at measurable rates yielded products with electronic spectra corresponding to that of B_{12r} (cob(II)alamin).[4,15]

Results and Discussion

Stoichiometry experiments dealing with the B_{12s}–U(VI) reaction (Table I), carried out with excess Co(I), indicate the consumption of nearly equimolar quantities of the two reagents, both in acetate buffers and in dilute $HClO_4$. Since the cobalt product is cob(II)alamin, the net reaction may be indicated schematically

$$U(VI) + Co(I) \rightarrow U(V) + Co(II) \qquad (1)$$

Departures from precise stoichiometry (10–20%) may reasonably be attributed to a (poorly) competing reduction of U(V) to U(IV), a secondary reaction that should be less important in our kinetic runs, which employed U(VI) in excess.

For the reactions with Eu(III) and Ti(IV), the inaccessibility of states below Eu(II) and Ti(III) in aqueous solution[16] allows us to infer net 1e changes in these cases as well.

Oxidation by Eu(III). Kinetic data for the B_{12s}–Eu^{3+} reaction are summarized in Table II. Rates are seen to be very nearly independent of $[H^+]$ and of concentrations of buffering species in solutions buffered by glycine and "MES", and in dilute $HClO_4$ as well, although there appears to be slight dependence on the nature of the supporting electrolyte. At higher pHs, and in solutions of "TES" buffers, however, reactions are accelerated by

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Table II. Representative Kinetic Data for the Oxidation of Vitamin B_{12s} (Cob(I)alamin) with Eu(III)[a]

pH	$[BH^+]$, M	[B], M	k,[b] $M^{-1}\,s^{-1}$
	A. "TES" Buffers		
7.38	0.010	0.010	108 (97)
7.67	0.0050	0.010	86 (85)
7.07	0.010	0.0050	117 (114)
7.93	0.0050	0.020	44 (50)
6.73	0.020	0.0050	119 (117)
7.33	0.0050	0.0050	114 (110)
7.37	0.020	0.020	90 (81)
7.41	0.050	0.050	72 (51)
7.72	0.0050	0.015	64 (71)
6.33	0.050	0.0050	99 (118)
	B. "MES" Buffers		
6.88	0.0050	0.020	91
5.85	0.020	0.010	92
	C. Glycine Buffers		
3.03	0.0050	0.020	48
2.50	0.010	0.010	52
	D. Dilute $HClO_4$, No Buffer		
3.8			62
1.5			58

[a] Temperature 25 °C; $\mu = 0.20$ M ($NaClO_4$); $[B_{12s}]_0 = 6 \times 10^{-5}$ to 10^{-4} M; $[Eu^{3+}] = 6 \times 10^{-4}$ to 1.3×10^{-3} M. [b] Second-order rate constants; values in parentheses were calculated from eq 3, by taking $k_{lim} = 124\ M^{-1}\,s^{-1}$, $K_A' = 8.3 \times 10^{-8}$ M, and $K_L = 9.3\ M^{-1}$ (see text).

increasing acidity but retarded by raising the concentration of buffering base, indicating that one of the reacting species (almost certainly Eu^{3+}) is being deactivated both by deprotonation and by ligation with the buffer. The combined effects of these competing equilibria on the overall rate may be expressed by (2),[17]

$$\text{rate} = \frac{k[H^+][Eu^{3+}]_T[B_{12s}]}{K_A + [H^+] + [TES]K_L(K_A' + [H^+])} \tag{2}$$

where $[Eu^{3+}]_T$ is the total concentration of added Eu(III), K_A is its acidity constant, [TES] is the concentration of added buffer, K_L is the association constant for the Eu(III)–TES complex, and K' is the acidity constant for this complex. Since K_A of Eu(III) (2×10^{-9})[18] falls well below the acidity range examined, the first term in the denominator may be neglected, and (2) may be simplified to (3). Least-squares refinement of the data in "TES" buffer yields a limiting specific rate: $k = 124 \pm 8\ M^{-1}\,s^{-1}$, $K_L = 9.3 \pm 2.1\ M^{-1}$, and $K_A' = (8 \pm 2) \times 10^{-8}$ M. Table II also compares observed rates with those calculated from (3).

$$k_{obsd} = \frac{\text{rate}}{[Eu^{3+}]_T[B_{12s}]} = \frac{k[H^+]}{[H^+] + [TES]K_L(K_A' + [H^+])} \tag{3}$$

The first coordination sphere of the active form of Eu(III) appears to consist wholly of water molecules, which have been shown generally to be ineffective in redox bridging,[19] and no appreciable kinetic contribution from $EuOH^{2+}$ was observed. The B_{12s}–Eu(III) reaction is therefore taken to proceed predominantly by an outer-sphere route. The limiting specific rate may then be used to estimate the rate of self-exchange for the B_{12s},B_{12r} system. Reported formal potentials are −0.379 V for Eu(II,III),[20] and −0.61 V for B_{12s},B_{12r},[21] whereas the estimated[22,23] self-exchange rate for the europium couple is 10^{-5}–$10^{-4}\ M^{-1}\,s^{-1}$. Since the B_{12s}–Eu(III) "cross-section" features only a moderate difference in potentials, Marcus's treatment[24] yields the approximate relationship

$$k_{Co,Eu} = (k_{11}k_{22}K)^{1/2} \tag{4}$$

where $k_{Co,Eu}$ refers to the cross-reaction, k_{11} and k_{22} refer to the self-exchange rates, and K is the equilibrium constant for the reaction. The calculated Co(I,II) self-exchange rate is $10^{4.8\pm0.5}\ M^{-1}\,s^{-1}$. This is a relatively high rate for a pair of first-row transition-metal centers[25] and probably reflects the minimal alterations in molecular geometry associated with electron transfer in this strongly conjugated system.[26]

Table III. Kinetic Data for the Oxidation of Vitamin B_{12s} (Cob(I)alamin) with $TiO(C_2O_4)_2^{2-}$ [a]

pH	[HOAc], M	$[OAc^-]$, M	$10^{-2}k_{obsd}$,[b] $M^{-1}\,s^{-1}$	$10^{-2}k_{calcd}$,[c] $M^{-1}\,s^{-1}$
4.56	0.010	0.010	0.46	0.52
4.51	0.020	0.020	0.69	0.74
4.53	0.040	0.040	0.99	1.06
4.56	0.080	0.080	1.69	1.71
4.54	0.120	0.120	2.5	2.4
4.53	0.160	0.160	3.1	3.1
4.21	0.020	0.010	1.28	1.18
3.98	0.030	0.010	2.2	2.1
3.81	0.040	0.010	3.0	3.2
3.60	0.060	0.010	6.1	5.8
3.48	0.080	0.010	8.2	8.3

[a] Temperature 25 °C, $\mu = 0.20$ M ($NaClO_4$); $[B_{12s}]_0 = 6 \times 10^{-5}$ to 9×10^{-5} M; $[Ti(IV)] = 3 \times 10^{-4}$ to 1×10^{-3} M. [b] Second-order rate constants. [c] Values calculated from eq 5 in text, taking $a = 2.73 \times 10^9\ M^{-3}\,s^{-1}$, $b = 1.20 \times 10^6\ M^{-2}\,s^{-1}$, and $c = 1.69 \times 10^3\ M^{-2}\,s^{-1}$.

Oxidation by Ti(IV). The oxalato complex, $TiO(C_2O_4)_2^{2-}$, was selected as a Ti(IV) oxidant presenting minimal precipitation problems in acetate buffers. Representative data for the B_{12s}–Ti(IV) reaction appear in Table III.

Reactions are seen to be strongly accelerated by H^+ and, less markedly, by added acetic acid. Rates, within the limited pH range 3.4–4.6, conform to (5), where $[Ti^{IV}]_T$ represents the total concentration of added Ti(IV). The implication here is that the reaction entails three paths. Each of the activated complex contains, in addition to the two redox partners, extra units of H^+ or acetic acid. Refinement of rate data according to (5) yields $a = (2.73 \pm 0.26) \times 10^9\ M^{-3}\,s^{-1}$, $b = (1.20 \pm 0.07) \times 10^6\ M^{-2}\,s^{-1}$, and $c = (1.69 \pm 0.05) \times 10^3\ M^{-2}\,s^{-1}$.

$$k_{obsd} = \frac{\text{rate}}{[Ti^{IV}]_T[B_{12s}]} = a[H^+]^2 + b[H^+] + c[HOAc] \tag{5}$$

Since the pH range in this series falls well below the recorded pK_A of B_{12s} (5.6 in 0.5 M KCl),[27] the reductant exists very nearly completely in its protonated form throughout. The three terms in (5) then pertain to different Ti(IV) species. The diprotonated (a) and monoprotonated (b) terms may be associated with the recognized elevation of the formal potential of Ti(III,IV) with decreasing pH, a trend that stems from the greater stabilization of the higher state by hydroxo or oxo coordination and that is reflected, in reverse, in many enhanced rates of reduction by

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(24) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(25) Recorded[22] self-exchange specific rates are $2 \times 10^{-5}\ M^{-1}\,s^{-1}$ for $Co(en)_3^{2+/3+}$, 4×10^1 for $Co(phen)_3^{2+/3+}$, and 10^3–10^4 for $Fe^{II,III}$(cyt *c*).

(26) It has been observed (Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647) that outer-sphere reductions of a variety of reagents by Eu^{2+} are 15–20 times as rapid as those by Cr^{2+}. An infrequently cited corollary of the Marcus formalism[24] is that given two redox couples with very nearly the same formal potentials (such as $Eu^{2+/3+}$ and $Cr^{2+/3+}$), relative rates for reduction of an external oxidant by the two lower states should correspond to those for oxidation of an external reductant by the two upper states (since both ratios are determined only by the relative rates of self-exchange). On this basis, the upper limit recorded here for the oxidation of B_{12s} by Cr^{3+} aq ($0.08\ M^{-1}\,s^{-1}$) is unexpectedly low. The observed inactivity of Yb^{3+}_{aq} may be attributed to the poorly oxidizing formal potential (ca. −1.15 V) of that lanthanide center.

(27) Rubinson, K. A.; Parekh, H. V.; Itabashi, E.; Mark, H. B., Jr. *Inorg. Chem.* **1983**, *22*, 458.

Table IV. Kinetic Data for the Oxidation of Vitamin B_{12s} (Cob(I)alamin) with Uranium(VI)[a]

buffer system	pH	$10^{-5}k$, $M^{-1}\ s^{-1}$
acetate–acetic acid	5.70	33
	5.23	45
	4.59	36
phthalate–biphthalate	5.28	33
	4.23	45
glycine–glycine-H^+	2.89	43
	2.53	39
	2.31	40
"MES"–"$MESH^+$"	6.43	0.28
	6.10	0.71
	5.82	0.85
	5.72	1.42

[a] Temperature 23.5 °C, $\mu = 0.20$ M ($NaClO_4$). Uranium(VI) (8×10^{-5} to 4×10^{-4} M) was added as $UO_2(ClO_4)_2$; $[B_{12s}]_0 = 3 \times 10^{-5}$ M; $[NaBH_4] = 5 \times 10^{-4}$ M; $[PdCl_4^{2-}] = 6 \times 10^{-5}$ M (see Experimental Section).

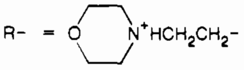
Ti(III) at higher pHs.[28] The [HOAc]-proportional term (c) may apply to interaction of acetic acid with the titanyl oxygen (a type of general-acid catalysis) or may arise from a protonated intermediate in which acetate occupies a coordination position at the Ti(IV) center.

Note that parameters a–c in (5) are combinations of association constants for preequilibria and specific rates for the various electron-transfer steps. In the absence of evidence for kinetic saturation, we cannot evaluate the individual contributing factors. Extension of this study to higher acidities (where complications associated with handling acidic solutions of B_{12s} in stop-flow apparatus are anticipated) might be instructive.

Oxidation by U(VI). The B_{12s}–UO_2^{2+} reaction is much more rapid than the others for which measurements were here carried out. The observed 1:1 stoichiometry indicates the primary reduction product to be U(V), even with Co(I) in large excess. This conclusion was unexpected, for its formal reduction potential, $E°(U^V \rightarrow U^{IV})$ (0.58 V),[29] implies quantitative conversion to U(IV). This situation brings to mind the reported formation of U(V) when UO_2^{2+} is reduced with Eu(II)[30] or Cr(II),[31] (although the latter reaction is complicated by the formation of a Cr(III)–U(V) complex). Selbin's suggestion[29] that extensive reorganization in the primary coordination sphere (resulting in a higher Franck–Condon barrier) severely retards the reduction of UO_2^+ to U^{4+}_{aq} but not the reduction of UO_2^{2+} to the structurally similar cation UO_2^+ appears to apply here. These relationships stand in contrast to those obtaining in the B_{12s} reductions of V(IV) and Mo(VI),[7] where major structural alteration accompanies gain of the first electron but only minor change is associated with acceptance of a second, resulting in increased rates of consumption of Co(I) as the reactions proceed.

Kinetic data for the B_{12s}–U(VI) reaction in several buffer systems are summarized in Table IV. The specific rate in carboxylate buffers is very nearly independent of both pH and the nature of the buffering species and appears to be a limiting value applicable to 23.5 °C and $\mu = 0.2$ M. The sulfonated buffer "MES" (4-morpholineethanesulfonic acid) is seen to inhibit the reaction severely, probably by converting U(VI) to a less reactive sulfonate-bound complex (represented as cation I), which is transferred to a much more active species (II) on protonation, leading to the acidity dependence observed in this medium ($k_{obsd} = 6.9 \times 10^{10}[H^+]$):

$$UO_2^{2+} + \text{“MES”} \rightarrow \underset{\text{I, inactive}}{[RSO_3\text{–}UO_2]^{2+}} \underset{pK_A < 5}{\overset{H^+}{\rightleftharpoons}} \underset{\text{II, active}}{[RSO_3\text{–}UO_2H]^{3+}} \quad (6)$$



Since the $[H^+]$ dependence exhibits no indication of kinetic saturation within the pH range studied, pK_A for the protonation of I may be taken to be less than 5.

The specific rate for this reaction ($4 \times 10^6\ M^{-1}\ s^{-1}$) in the other buffer systems may be compared to that estimated by the simplified Marcus treatment (eq 4) by using the recorded formal potential for $UO_2^{+/2+}$ (+0.05 V),[32] the reported self-exchange rate for this couple ($10^2\ M^{-1}\ s^{-1}$),[33] and the Co(I,II) self-exchange rate estimaed from the B_{12s}–Eu^{3+} reaction.[34] The calculated value, $10^8\ M^{-1}\ s^{-1}$, is greater than that observed by $10^{1.4}$, a discrepancy similar in direction to, although of somewhat less magnitude than, that encountered by Ekstrom[30] in comparing calculated and observed specific rates for the reduction of UO_2^{2+} with U^{3+}. The hazards of applying this treatment to cross-reactions having large $\Delta E°$ values have been emphasized by Chou and co-workers.[22,35,36]

An analogous comparison may be based on the lower limit here noted for the B_{12s}–Cu^{2+} reaction ($5 \times 10^6\ M^{-1}\ s^{-1}$). Using the very low upper limit reported for the rate of reduction of $Co(en)_3^{3+}$ by Cu^+ ($4 \times 10^{-4}\ M^{-1}\ s^{-1}$),[37] the $\Delta E°$ value for that reaction (0.41 V), and the rate of $Co(en)_3^{3+/2+}$ self-exchange ($2 \times 10^{-5}\ M^{-1}\ s^{-1}$),[22] we may calculate the $Cu^{2+/+}$ self-exchange to proceed more slowly than $10^{-9}\ M^{-1}\ s^{-1}$ in the absence of bridging ligands. This, in turn, leads to an estimate of $6 \times 10^3\ M^{-1}\ s^{-1}$ as an upper limit of the B_{12s}–Cu^{2+} reaction ($\Delta E° = 0.67$ V) if only an outer-sphere path were to contribute. The difference between the latter value and our recorded limit is consistent with a predominant inner-sphere component for this oxidation.[38]

In sum, the present study constitutes one of the few to date dealing with the reactions of B_{12s} with oxidants that are unequivocally 1e acceptors. Although the kinetic peculiarities observed mirror mainly the metal oxidants taken and only secondarily the properites of the Co(I) center, one should not overlook advantages in working with this reductant, reflecting (a) the ease with which it may be generated, (b) its strongly negative formal potential, and (c) its very intense absorption maxima, which allow us to examine the behavior of weakly absorbing metal ions in media that would lead to the precipitation if they were taken at concentrations where their spectra could be observed directly.

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Registry No. U^{6+}, 22541-40-8; Eu^{3+}, 22541-18-0; $TiO(C_2O_4)_2^{2-}$, 16041-00-2; vitamin B_{12s}, 18534-66-2.

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(28) See, for example: Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 1103.

(29) Selbin, J.; Ortego, J. D. *Chem. Rev.* **1969**, *69*, 657. The listed potential applies to a 1 M solution in $HClO_4$ at 25 °C. It is subject to slight variation with changes in pH or the addition of ligating species, but such changes would not be expected to nullify the calculated driving force ($\Delta E° > 1.0$ V) associated with the B_{12s}–U(V) reaction.

(30) Ekstrom, A.; Johnson, D. A. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2557.

(31) (a) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1962**, *1*, 368. (b) Gordon, G. *Inorg. Chem.* **1963**, *2*, 1277. (c) Ekstrom, A. *Inorg. Chem.* **1973**, *12*, 2455. (d) Ekstrom, A.; Farrar, Y. *Inorg. Chem.* **1972**, *11*, 2610.

(32) Latimer, W. M. *Oxidation Potentials*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952; p 304.

(33) Masters, B. J; Schwarz, L. L. *J. Am. Chem. Soc.* **1961**, *83*, 2620.

(34) For this calculation, the formal potential of B_{12s} at pH 2 (–0.50 V)[27] was used.

(35) In comparing the reactivities of B_{12s} toward Eu^{3+} and UO_2^{2+}, we have ignored contributions from electrostatic work terms. Evaluations of such contributions are complicated by uncertainty in the structure and geometry of the transition states. However, within the pH ranges examined, B_{12s} ($pK_A = 5.6$)[27] exists either as an uncharged species or a unipositive ion in which the positive center lies well removed from the electron-transfer site. Hence, these contributions are expected to be small. The maximum error resulting from neglect of work terms in the two systems may be calculated[36] by assuming a +1 charge centered at Co(I) and taking the distance of closest approach as 1.65 Å for Eu^{3+}–B_{12s} and 1.35 Å for UO_2^{2+}–B_{12s}. On this basis, the work terms for the two systems differ by less than 0.90 kcal/mol, corresponding to a kinetic factor below 2.

(36) See, for example: (a) Phillips, J.; Haim, A. *Inorg. Chem.* **1980**, *19*, 76. (b) Singh, A. N.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 1236.

(37) Parker, O. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1968.

(38) A reviewer called our attention to this point.