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Electron Transfer. 71. Reductions of Inorganic Cobalt(III) Complexes by Vitamin B_{12r} (Cob(II)alamin)[1]

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Vitamin B_{12r} (cob(II)alamin), the Co(II) derivative of vitamin B_{12}, reacts, via electron transfer, with the chloro, bromo, iodo, azido, thiocyanato (N-bound), and pyrazine derivatives of $(NH_3)_5Co^{III}$, as well as with $(bpy)_3Co^{3+}$, yielding, in each case, aquocobalamin and Co^{2+}. Specific rates for reduction of the –NCS and pyrazine complexes are independent of acidity within the range $[H^+] = 0.01–0.5$ M, whereas rate laws for each of the other reactions feature prominent inverse-$[H^+]$ terms that are taken to pertain to reaction with the deprotonated form of B_{12r} (pK_A 2.9). Reduction of $(bpy)_3Co^{3+}$ is necessarily an outer-sphere process, whereas detection of a transient iodocobalamin product in the very rapid reduction of $Co(NH_3)_5I^{2+}$ points to an inner-sphere path (with iodo bridging) for the latter reaction and, by implication, for the corresponding bromo, chloro, azido, and thiocyanato reactions as well. The ratio of acid-independent specific rates for reductions of the $-N_3$ and –NCS complexes is 1/8, the lowest such ratio thus far reported, indicating that B_{12r} is the softest of the available reducing metal centers. Reactions of B_{12r} with carboxylato and ring-bound pyridine derivatives of $(NH_3)_5Co^{III}$ are immeasurably slow, even when the organic ligands are among the most effective known for reductions by Cr^{2+} and Eu^{2+}. The structure of B_{12r} precludes reduction via a chelated transition state, whereas its formal potential (+0.30 V) rules out reaction via the chemical mechanism unless the mediating ligand is especially easily reduced (e.g., a substituted pyrazine). The ratio of specific rates for the reduction of $(en)_3Co^{3+}$ by cob(I)alamin and cob(II)alamin has been found to exceed 6×10^8, a ratio that appears to be consistent with the Marcus model for outer-sphere reactions. In contrast, the corresponding B_{12s}/B_{12r} rate ratio for reductions of $HClO_3$ is only 10^4, thus suggesting an inner-sphere path for the $B_{12r}–HClO_3$ reaction.

Vitamin B_{12r} (cob(II)alamin), the cobalt(II) derivative of vitamin B_{12}, is a reducing agent having a formal potential (+0.30 V at pH 1)[2] near that for $Ru(NH_3)_6^{2+}$. Since the Co(II) center is coordinatively unsaturated (5-covalent) in acid solution and, in addition, features a substitution-labile axial substituent (H_2O),[3] this reductant would be expected to utilize the inner-sphere path in electron-transfer reactions with oxidants having appropriate bridging groups. Indeed, Heckman and Espenson[4] have demonstrated the operation of such a path in the oxidation of B_{12r} by I_2.

The present work deals with the oxidation of B_{12r} by a series of $(NH_3)_5Co^{III}$ derivatives in which the mediating characteristics of the sixth ligand vary considerably. Although we too observe evidence for an inner-sphere path, we find a much more limited response to organic bridging units than has been noted for reductions by the aquo ions of Cr^{2+},[5] Eu^{2+},[6] and Ti^{3+}.[7] Our results complement those of an earlier study[8] of reductions by diaquocob(II)aloxime at higher pH values, but there are differences in detail.

Experimental Section

Materials. This(bipyridyl)cobalt(III) perchlorate[9] and the thiocyanato,[10] azido,[11] and iodo[12] derivatives of $(NH_3)_5Co^{III}$ (perchlorate salts) were prepared as described. Solutions of the azido and iodo complexes were kept in blackened vessels to minimize photochemical decomposition. The remaining cobalt(III) complexes were available from previous studies.[6,13] Lithium perchlorate, for use in kinetic experiments, was prepared as described.[14] Hydroxocobalamin hydrochloride (Sigma Chemicals) was used as received and was converted to cob(II)alamin by reduction with zinc amalgam as described.[15] All reactions were carried out under N_2 in distilled water that had been previously boiled and purged with oxygen-free N_2 for at least 4 h.

Table I. Stoichiometries of the Reactions of Cob(II)alamin (B_{12r}) with Pentaamminecobalt(III) Complexes

oxidant	$[H^+]$, M	$10^5 \times [B_{12r}]$, M	$10^5 \times$ [Ox], M	$10^5 \times \Delta[B_{12r}]$, M	$\Delta[B_{12r}]/\Delta[Ox]$
$Co(NH_3)_5I^{2+}$ [a]	0.11	4.05	1.90	1.93	1.02
		4.05	2.67	2.70	1.02
		6.63	2.78	2.67	0.96
		6.63	3.49	3.28	0.94
		8.10	2.67	2.89	1.08
		8.10	3.82	3.66	0.96
$Co(NH_3)_5Br^{2+}$ [a]	0.12	4.10	2.43	2.60	1.07
		8.10	2.40	2.45	1.01
		8.10	4.80	4.57	0.95
$Co(NH_3)_5N_3^{2+}$ [b]	0.030	8.10	2.50	2.59	1.04
		8.10	5.00	5.50	1.10
$Co(NH_3)_5NCS^{2+}$ [b]	0.020	8.20	3.40	3.12	0.92

[a] Measurements made at 350 nm. [b] Measurements made at 470 nm.

Stoichiometric Studies. Stoichiometries of four of the more rapid reactions, taking B_{12r} in excess, were determined by adding a measured deficiency of the oxidant to a known excess of B_{12r}, waiting 30–100 min for completion of the reaction,[16] and then measuring either the increase

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[2] See, for example: Lexa, D.; Saveant, J.-M. *Acc. Chem. Res.* **1983**, *16*, 235. This value is strongly pH dependent. Moreover, redox reactions by B_{12r} may be complicated by the equilibrium between the internally benzimidazole-coordinated ("base-on") and noncoordinated benzimidazole ("base-off") forms.

[3] The lability of axial substituents in cob(III)alamin derivatives has been demonstrated by: Thusius, D. *J. Chem. Soc.* **1971**, *93*, 2629. Ligand exchange in the corresponding Co(II) complexes, for which ligand field stabilization is less marked, should be even more rapid.

[4] Heckman, R. A.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 38.

[5] See, for example: (a) Taube, H.; Gould, E. S. *Acc. Chem. Res.* **1969**, *2*, 321. (b) Thamburaj, P. K.; Loar, M.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1946.

[6] Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639.

[7] (a) Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1975**, *14*, 873. (b) Ram, M. S.; Martin, A. H.; Gould, E. S. *Ibid.* **1983**, *22*, 1103.

[8] Adin, A.; Espenson, J. H. *Inorg. Chem.* **1972**, *11*, 4.

[9] Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570.

[10] Carlin, R. L.; Edwards, J. O. *J. Inorg. Nucl. Chem.* **1958**, *6*, 217.

[11] Linhard, M.; Flygare, H. *Z. Anorg. Allg. Chem.* **1950**, *262*, 328.

[12] Haim, A.; Taube, H. *J. Am. Chem. Soc.* **1963**, *85*, 495. Solutions of the iodo complex generally contain some of the corresponding aquopentaammine complex, resulting from aquation. Concentrations of the iodo complex in such solutions were therefore determined spectrophotometrically ($\epsilon_{388} = 2.7 \times 10^3$ M^{-1} cm^{-1}) just prior to kinetic runs.

[13] (a) Wu, M.-Y.; Paton, S. J.; Fanchiang, Y.-T.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 326. (b) Gould, E. S.; Johnson, N. A.; Morland, R. B. *Ibid.* **1976**, *15*, 1929. (c) Hua, L. H.-C.; Balahura, R. J.; Fanchiang, Y.-T.; Gould, E. S. *Ibid.* **1978**, *17*, 3692.

[14] Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

[15] Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 3689.

[16] Reliable stoichiometries of the slower reactions could not be determined since consumption of B_{12r} by traces of air slowly leaking into the vessel became competitive with the primary reaction.

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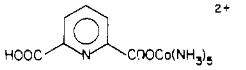
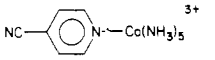
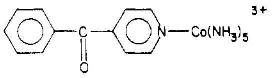
Table II. Representative Kinetic Data for Reactions of Vitamin B_{12r} (Cob(II)alamin) with $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5NCS^{2+}$ [a]

$10^5[Ox]$, M	$[H^+]$	k_{obsd} [b]	k_2 [c]
	$Co(NH_3)_5Br^{2+}$		
2.60	0.50	0.48	1.85
2.78		0.57	2.0
5.56		1.14	2.0
11.10		2.5	2.2
2.60	0.40	0.67	2.6
2.60	0.30	0.88	3.3
2.69	0.21	0.92	3.4
2.69	0.106	1.41	5.2
2.69	0.064	2.2	8.2
2.69	0.034	4.0	14.8
2.69	0.017	7.4	28
	$Co(NH_3)_5NCS^{2+}$		
25.6	0.52	1.40	0.54
54.4	0.50	2.9	0.52
108.0	0.50	5.2	0.48
54.4	0.25	2.9	0.52
31.2	0.12	1.44	0.53
54.4	0.12	2.8	0.52
54.4	0.064	3.3	0.60
40.0	0.031	2.6	0.64
40.0	0.011	2.5	0.63

[a] Reactions were carried out at 25 °C; the supporting electrolyte was $LiClO_4$ ($\mu = 0.50$ M). $[B_{12r}]_0 = 4.0 \times 10^{-5}$ M throughout. [b] Pseudo-first-order rate constants ($s^{-1} \times 10^2$) $= -d[B_{12r}]/dt[B_{12r}]^{-1}$. [c] Second-order rate constants ($M^{-1}\ s^{-1} \times 10^{-2}$), obtained by dividing k_{obsd} by [Ox].

Table III. Specific Rates for Oxidation of Vitamin B_{12r} (Cob(II)alamin) with Cobalt(III) Complexes (25 °C; $\mu = 0.51$ M)

oxidant	k, $M^{-1}\ s^{-1}$
$(NH_3)_5CoCl^{2+}$	$(0.56 \pm 0.20) + (0.40 \pm 0.01)[H^+]^{-1}$
$(NH_3)_5CoBr^{2+}$	$(93 \pm 28) + (47 \pm 1)[H^+]^{-1}$
$(NH_3)_5CoI^{2+}$	5.9×10^5 (in 0.10 M H^+)[a] 2.9×10^5 (in 0.30 M H^+)[a]
$(NH_3)_5CoN_3^{2+}$	$(6.8 \pm 0.7) + (0.60 \pm 0.01)[H^+]^{-1}$
$(NH_3)_5CoNCS^{2+}$	55 ± 5
$(bpy)_3Co^{3+}$	$(0.052 \pm 0.001)[H^+]^{-1}$
$(pyrazine)Co(NH_3)^{53+}$	1.8
$(en)_3Co^{3+}$	$<10^{-3}$ [b]
$(maleato)Co(NH_3)_5^{2+}$	$<10^{-3}$
$(pyruvato)Co(NH_3)_5^{2+}$	$<10^{-3}$
$C_6H_5C({=}O)COOCo(NH_3)_5^{2+}$	$<10^{-3}$
	$<10^{-3}$
$C_6H_5CH_2SCH_2COOCo(NH_3)_5^{2+}$	$<10^{-3}$
	$<10^{-3}$
	$<10^{-3}$
$(NH_3)_5CoF^{2+}$	$<10^{-3}$

[a] 21 °C. [b] k for reaction of $(en)_3Co^{3+}$ with B_{12s} (cob(I)alamin) was estimated as $5.8 \times 10^5\ M^{-1}\ s^{-1}$ at $[H^+] = 0.010$ M and $2.2 \times 10^5\ M^{-1}\ s^{-1}$ at $[H^+] = 0.38$ M (21 °C; $\mu = 0.5$ M).

in absorbance at 350 nm (for reactions of $Co(NH_3)_5I^{2+}$ and $Co(NH_3)_5Br^{2+}$) or the decrease in absorbance at 470 nm (for reactions of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5NCS^{2+}$). These changes, after small corrections for the slow loss of B_{12r} in the absence of coreagent, were compared to those observed when B_{12r} was treated with excess oxidant. Representative results appear in Table I.

Kinetic Studies. Rates were estimated from measurements of changes in absorbance made by using a Cary 14 or Beckman Model 5260 recording spectrophotometer or a Durrum-Gibson stopped-flow spectrophotometer. Reductions of the iodo-, the azido-, and the thiocyanato-substituted oxidants were monitored by following the disappearance of B_{12r} at 470 nm. Other reactions were studied by measuring the appearance of cob(III)alamin (B_{12a}) at 350 nm.[17] Acidities were regulated by addition of known concentrations of $HClO_4$, and total ionic strength was maintained near 0.50 M by addition of $LiClO_4$.[18] Reactions were first order each in oxidant and B_{12r} but were carried out under pseudo-first-order conditions with the oxidant in greater than 10-fold excess. Conversions were generally followed for at least 5 half-lives. Rate constants 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 checked to better than 7%. Temperatures were kept at 25.0 ± 0.2 °C for all experiments on the Cary and Beckman instruments, whereas some reactions of the iodo-substituted oxidant were carried out on the stopped-flow instrument at 15 and 21 °C.

Solutions from each of the reactions carried out with the oxidant in excess exhibited spectral characteristics corresponding to those of aquocob(III)alamin.[4]

When the reaction of the iodo complex was followed at 555 nm, a second decay, which was considerably slower than the primary reaction, was evident. The specific rate for this transformation was independent of the initial concentrations of oxidant and reductant but depended to a slight extent on acidity ($34\ s^{-1}$ in 0.30 M H^+, $42\ s^{-1}$ in 0.10 M H^+; 25 °C, $\mu = 0.50$ M).[19,20]

The reactions of B_{12r} with $(NH_3)_5CoF^{2+}$, and with carboxylato and substituted pyridine derivatives of $(NH_3)_5Co^{III}$, were so slow that the slight absorbance changes in the presence of these oxidants were indistinguishable from the very gradual changes resulting from the consumption of B_{12r} by adventitious traces of O_2. In contrast, the reactions of each of these oxidants with B_{12s} (cob(I)alamin), the Co(I) analogue of B_{12r}, were too rapid to follow with our stopped-flow equipment.

Results and Discussion

The very close approach to 1/1 stoichiometry exhibited by the more rapid reactions (Table I), in conjunction with the observed spectrum of the principal absorbing product, indicates that the net changes may be represented in a straightforward manner (eq 1) and that, in the reactions of the azido and thiocyanato complexes, reduction of the liberated ligand by B_{12r} is negligible on the time scale for the primary reactions.[21] Analogous stoichiometry may be assumed for the slower reactions.

$$Co(NH_3)_5X^{2+} + [Co^{II}(corrinH)]^+ + 4H^+ \rightarrow [Co^{III}(corrin)]^+ + Co^{2+} + 5NH_4^+ + X^- \quad (1)$$

Representative kinetic data for two of the oxidations, those involving $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5NCS^{2+}$, appear in Table II. Note that the bromo reaction is strongly acid dependent whereas the rate of the thiocyanato reaction is very nearly constant within the acidity range examined. Specific rates for all oxidants in the series are summarized in Table III.

A number of the more rapid reactions feature prominent inverse-$[H^+]$ terms in their rate laws, and for the bipyridyl-sub-

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(17) In the case of the reduction of $Co(bpy)_3^{3+}$, the high absorbance of this species at 350 nm necessitated addition of this complex to the reference spectrophotometer cell (as well as to the reaction mixture) in order to obtain useful readings on the absorbance scale.

(18) Attempts were made to extend the pH range of these measurements by carrying out the reactions in glycine buffers. Although reproducible kinetic curves were obtained, it was found that addition of as little as 10^{-3} M glycine (while keeping pH constant) retarded several of the reactions by 30% or more. This effect became more serious as pH was increased.

(19) Evidence suggesting an analogous secondary reaction in the oxidation of B_{12r} by $Co(NH_3)_5N_3^{2+}$ could be obtained by carrying out the primary reaction at pH 8–10. When the reaction was monitored at 550 nm, a second decay was noted. The kinetic characteristics of the latter ($k = 0.033 \pm 0.013\ s^{-1}$, $\mu = 0.5$ M) were poorly reproducible.[20] This second decay was not observed when the primary transformation was carried out at pH 0.7–2.0, the acidity range used in our kinetic study of the redox reactions.

(20) The specific rate of aquation of azidocob(III)alamin has been reported as $0.03 \pm 0.02\ s^{-1}$ at pH 9.0 ($\mu = 0.054$ M): Randall, W. C.; Alberty, R. A. *Biochemistry* **1967**, *6*, 1520.

(21) In accord with this conclusion, we find that reduction of hydrazoic acid by cob(II)alamin proceeds at a specific rate less than $10^{-3}\ M^{-1}\ s^{-1}$ at 25 °C. In contrast, cob(I)alamin is found to reduce HN_3 at a specific rate near $1.6 \times 10^2\ M^{-1}\ s^{-1}$ at pH 2.4 ($\mu = 0.1$ M).

stituted oxidant, only this term appears. Since the latter complex lacks acidic hydrogens, the $[H^+]^{-1}$ dependency here must be associated with deprotonation of the reductant, B_{12r} (pK_A 2.9).[2] A similar conclusion may be taken to apply to the $[H^+]^{-1}$ terms for the halo and azido oxidants.[22,23] Division of the inverse-[acid] specific rates by K_A for B_{12r} yields bimolecular rate constants for reactions of these oxidants with the deprotonated form of cob(II)alamin; the resulting values are 3×10^2 M^{-1} s^{-1} for the chloro complex and 4×10^4, 5×10^2, and 40 M^{-1} s^{-1} for the bromo, azido, and bipyridyl complexes.

It is quite clear that both outer- and inner-sphere mechanism operate within this series. For $(bpy)_3Co^{3+}$, which is devoid of "lead-in" donor groups, the outer-sphere path is mandatory. In contrasts, there is strong evidence pointing to a bridged transition state with halogen transfer for reduction of the unusually reactive iodo complex. The primary reaction here is followed by a unimolecular decay, which may be monitored easily at 555 nm. The specific rate of the latter reaction (42 s^{-1} at 25 °C, $[H^+] = 0.10$ M, $\mu = 0.5$ M is in reasonable agreement with the value (37 s^{-1} at 25 °C, $[H^+] = 0.10$ M, $\mu = 0.1$ M) reported by Heckman and Espenson[4] for aquation of the iodocobalt(III) complex iodocobalamin, formed by reaction of B_{12r} with I_2. Moreover, the absorbance decrease associated with the unimolecular decay corresponds closely to that calculated from the difference in molar adsorptivities for iodo- and aquocobalamin at 555 nm.[24-26] Reduction of the iodo oxidant may then be represented as sequence (2)-(3). Detection of an analogous ligand-substituted species

$$(NH_3)_5CoI^{2+} + Co^{II}(corrin) \xrightarrow{k > 10^5\ M^{-1}\ s^{-1}} Co^{III}(corrin)(I) \quad (2)$$

$$Co^{III}(corrin)(I) \xrightarrow{42\ s^{-1}} Co^{III}(corrin)(H_2O) + I^- \quad (3)$$

in the remaining pentaamminecobalt(III) reductions does not appear to be feasible, for in each case, the sluggishness of the primary reaction precludes accumulation of an appreciable concentration of this product.[19] Nevertheless, the kinetic advantage enjoyed by the chloro-, bromo-, thiocyanato-, and azido-substituted oxidants over the bipyridyl complex indicates that with these four pentaammines, as with the iodo complex, inner-sphere contributions play a dominant role.

It has been pointed out by Adin[8] that the rate ratio for the inner-sphere reduction of $(NH_3)_5CoN_3^{2+}$, as compared to that for $(NH_3)_5CoNCS^{2+}$, may be taken as a reflection of the hardness of the reducing center, i.e. that this ratio lies near 10^4 for reductions by Cr^{2+} but drops nearly to unity for reductions by $Co(CN)_5^{3-}$.[27] Although such a comparison in the present system is complicated by the presence of two terms in the rate law for the azido complex, the ratio of the [acid]-independent terms, which pertains to reductions by the protonated forms of B_{12r}, is seen to lie near 1/8. This appears to be the first reported instance in which this ratio falls well below unity, and we thus conclude that B_{12r} is the softest of the avialable reducing metal centers, an inference that is in accord also with the very large rate ratio observed here for oxidations by the iodo and chloro derivatives of $(NH_3)_5Co^{III}$.

A striking aspect of the present study is the lack of kinetic response by B_{12r} to the incorporation of organic bridging groups into the oxidizing center. Among the oxidants that react immeasurably slowly with cob(II)alamin under our conditions are the $(NH_3)_5Co^{III}$ derivatives of maleic, pyruvic, phenylglyoxylic, and 2,6-pyridinedicarboxylic acids and the corresponding ring-bound complexes of 4-benzoyl- and 4-cyanopyridine. The organic ligands in this group are among the most potent inner-sphere mediators known for reductions by Cr^{2+} and Eu^{2+}.[6,13,25] Their lack of effectiveness in reactions of B_{12r} is, however, not wholly unexpected. The high rates for the maleato and 2,6-pyridinedicarboxylato complexes (with aquo reductants) reflect chelation in the transition states, but such chelation requires two substitution-labile sites in cis positions on the reduction center, a feature absent from all cobalamin species. The remaining powerfully mediating organic ligands, α-keto carboxylates and 4-substituted pyridines, are thought to operate via preliminary reduction of the ligand to yield a radical cation, which then undergoes internal electron transfer to the oxidizing center (the "chemical mechanism").[29] It has been emphasized[7a] that this mechanistic variation assumes significance only when the potential of the reducing center approaches that for 1e reduction of the mediating ligand and that it is therefore rarely, if ever, observed with the weaker reductants Fe(II), Cu(I), and Ti(III). Cob(II)alamin ($E° = +0.30$ V)[2] may be considered to fall in the latter category.[30] Note, however, that incorporation of bound pyrazine, a ligand featuring both a relatively soft lead-in center and a readily reducible[31] ring system, elevates the rate of reduction by B_{12r} to a value that is measurable by our methods.

Cob(I)alamin, the Co^I analogue of B_{12r}, reacts with each of the $(NH_3)_5Co^{III}$ complexes in Table III at a rate too great to be evaluated by the usual stopped-flow technique. However, the specific rate for reduction of $Co(en)_3^{3+}$, one of the most sluggish of the known Co^{III} oxidants,[32] has been estimated as 5.8×10^5 M^{-1} s^{-1} (at 21 °C and pH 2), which allows us to calculate lower limit of 6×10^8 for the ratio of reactivities of B_{12s} and B_{12r} with a common outer-sphere oxidant. The difference in the formal potentials of the two reductants is 0.78 V,[2] corresponding, by the model of Marcus,[33] to a $10^{6.5}$-fold difference in specific rates. In addition, collations by Lexa[2] indicate that self-exchange in the B_{12s}-B_{12r} system is much more rapid than that in the B_{12r}-B_{12a} system, a circumstance that should further favor reduction by B_{12s}. The lower limit for the B_{12s}/B_{12r} ratio pertaining to reactions with $(en)_3Co^{3+}$ thus appears to be consistent with the Marcus model, in contrast to the corresponding rate ratio (only 10^4) for reductions of $HClO_3$.[15] The difference in ratios for the two oxidants confirms, by comparison, the suggestion[15] that the B_{12r}-$HClO_3$ reaction proceeds mainly by an inner-sphere path, but further comparisons of this type are obviously desirable.

Registry No. $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5Br^{2+}$, 14970-15-1; $Co(NH_3)_5I^{2+}$, 15392-08-2; $Co(NH_3)_5N_3^{2+}$, 14403-83-9; $Co(NH_3)_5NCS^{2+}$, 14970-18-4; $Co(NH_3)_5(pyrazine)^{3+}$, 59389-55-8; cob(II)alamin, 14463-33-3.

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(22) Although these pentaammines are faintly acidic, the observed inverse-[acid] specific rates, when divided by the estimated K_a values for such complexes ($\sim 10^{-14}$ M),[23] yield hypothetical bimolecular rate constants in excess of the diffusion-controlled limit.

(23) Pearson, R. G.; Basolo, F. *J. Am. Chem. Soc.* **1956**, *78*, 4878.

(24) Typically, at 15 °C with $[B_{12r}] = 7.9 \times 10^{-5}$ M, $[(NH_3)_5CoI^{2+}] = 3.2 \times 10^{-4}$ M, and $[H^+] = 0.10$ M, iodocobalamin is formed at a pseudo-first-order specific rate of 114 s^{-1} but decays at a specific rate of 18.9 s^{-1}, corresponding[25] to a maximum concentration of iodocobalamin of 5.5×10^{-5} M. The observed decrease in optical density, in a 2.0-cm cell, is found to be 0.34 unit, corresponding to a difference in extinction coefficients of 3.1×10^3 M^{-1} cm^{-1} for iodo- and aquocobalamin at 555 nm. The latter value is in excellent agreement with the difference 3.2×10^3 M^{-1} cm^{-1}, obtained from comparison of the spectra of aquo- and iodocobalamin[26] in 0.10 M $HClO_4$.

(25) See, for example: Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill, New York, 1981; p 66.

(26) Iodocobalamin was prepared in solution by addition of 8×10^{-5} M aquocobalamin to 0.8 M KI. See, for example: Pratt, J. M.; Thorp, R. G. *J. Chem. Soc. A* **1966**, 187.

(27) See, for example: Candlin, J. P.; Halpern, J.; Nakamura, S. *J. Am. Chem. Soc.* **1963**, *85*, 2517.

(28) Gould, E. S. *J. Am. Chem. Soc.* **1974**, *96*, 2373.

(29) See, for example: (a) Srinivasan, V. S.; Singh, A. N.; Wieghardt, K.; Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 2531. (b) Goli, U. B.; Gould, E. S. *Ibid.* **1984**, *23*, 221.

(30) Diaquocob(II)aloxime, the structure and formal potential (+0.36 V, 0.1 M $NaClO_4$)[4] of which are very similar to those of B_{12r}, has likewise been found to react immeasurably slowly with the organic derivatives of $(NH_3)_5Co^{III}$ listed in Table III (Balasubramanian, P. N., unpublished experiments, 1983).

(31) Klatt, L. N.; Rouseff, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 7295. The data of these authors leads to a formal potential of -0.020 V (vs. NHE) for pyrazine in 1.0 M $HClO_4$.

(32) See, for example: Loar, M. K.; Sens, M. A.; Loar, G. W.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 330.

(33) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 866, 879. It is assumed that an increase in ΔG^* resulting from an increase in the standard potential of the reductant is half the increase in $\Delta G°$. (See, for example: Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557.)