unidentified oil followed closely by the yellow complex I. Evaporation of the solvent, followed by slow sublimation at room temperature under high vacuum to a cold finger cooled to 10°, yielded *ca.* 5 mg of pure, crystalline I, mp 133–135° (open capillary). Infrared spectrum (CS_2 solution): 2585 (vs), 2535 (vs), 2290 (w), 2125 (m), 1730 (w), 1445 (s), 1265 (w), 1100 (m), 1010 (m), 915 (m), 845 (w), 825 (vs), 755 (m), 705 (m) cm^{-1}.

Continued elution of the silica gel column with CH_2Cl_2–hexane mixtures resulted in the isolation of the following species as previously reported:[2] $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$, $[Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})_2]^{2-}$, and $B_9CH_{10}^-$.

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Registry No. I, 52540-76-8; $B_{10}H_{12}C[N(CH_3)_3]$, 12373-48-7.

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Correcting an Error. Effect of Perchlorate Ion on Hg^{2+}-Promoted Hydrolysis of Cobalt(III)-Coordinated Glycine Esters

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The recent report[1] that high concentrations of ClO_4^- change the mechanism of hydrolysis of glycine ethyl ester in *cis*-$[Co(en)_2X(glyOEt)]^{2+}$ ions (X = Cl, Br) following removal of X with Hg^{2+} came as a surprise to us since similar experiments in our hands on the same[2] and related[3] compounds had failed to suggest any change in mechanism on varying the electrolyte. Normally, removal of halide as HgX^+ results in the exclusive entry of the carbonyl oxygen into the coordination sphere to form a chelated glycine ester intermediate.[2-4] This intermediate subsequently hydrolyzes by an acid-independent pathway (pH ≤3) with acyl–oxygen bond rupture[5] and without opening of the chelate ring. This is represented by Scheme I. The recent publication[1] claims that at high ClO_4^- concentrations (≥4 *M*) a significant amount of the aquo monodentate ester complex $[Co(en)_2(H_2O)(glyOEt)]^{3+}$ is formed and that this compound is relatively inert and only slowly ($t_{1/2}$ = 23 min) reverts to the chelated ester intermediate by loss of bound water. (See Scheme II.) This claim is contrary to our experience with closely related aquo-β-alanine isopropyl ester[6] and *cis*-aquoglycineamide[7] complexes, and since it was largely based on rather unconvincing pmr results, it seemed important to repeat the experiments. This note reports our results.

Experimental Section

The $[Co(en)_2X(glyOEt)]Br_2$ (X = Cl, Br) compounds were prepared by standard procedures;[2] $[Co(en)_2(glyOEt)](ClO_4)_3$ was prepared using dry acetone instead of methanol as in a previously reported method.[8] All other reagents were Analar grade. $Hg(ClO_4)_2$ solutions in H_2O or D_2O were made up as required using HgO and concentrated $HClO_4$ or $DClO_4$. Kinetic data were collected on a Gilford 2400 spectrophotometer (487 nm) and on a Jeol Model JNH 4H-100 spectrometer, at 32°. Chromatographic analyses used Dowex 50W-X2 ion-exchange resin and 1 *M* $NaClO_4$ as eluent.

Table I. Spectrophotometric Rate Data[a]

$[Hg(ClO_4)_2]$, *M*	$[NaClO_4]$, *M*	k_{obsd}, min^{-1}	Comments
	(a) Following Removal of Bromide from *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$		
0.4	0.8	0.53	Total OD change = 0.085
0.4	0.8	0.58	
0.4	3.4	0.17	
0.4	3.4	0.17	
0.4	3.4	0.17	
0.4	3.4	0.16	Total OD change = 0.089
	(b) $[Co(en)_2(glyOEt)](ClO_4)_3$		
0.4	0	0.55	
0.4	0	0.26	D_2O–$DClO_4$ solvent
0.4	0.8	0.42	Total OD change = 0.084
0.4	0.8	0.47	
0.4	3.4	0.18	
0.2	3.4	0.18	
0.4	3.4	0.18	
0.4	3.6	0.060	D_2O–$DClO_4$ solvent

[a] At 32°, 487 nm, [Co] = 0.018 or 0.009 *M*, $[HClO_4]$ = 0.2 *M*; 0.1-OD slide wire.

Table II. Pmr Rate Data in D_2O[a]

$[DClO_4]$, *M*	$[Hg(ClO_4)_2]$, *M*	$[NaClO_4]$, *M*	k_{obsd}, min^{-1}
	(a) Following Removal of Bromide from *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$		
0.1	0.3	0.8	0.30
0.1	0.4	3.6	0.07
0.2	0.3	3.8	0.07
	(b) $[Co(en)_2(glyOEt)](ClO_4)_3$		
0.2	0.4	0	0.28
0.2	0.4	3.6	0.055
0.2	0.4	3.6	0.066,[b] 0.060[c]
0.1	0.3	3.8	0.066

[a] At 32° and [Co] ≈ 0.1–0.2 *M*. [b] CH_3 of ethanol. [c] CH_3 of ethyl ester.

Results and Discussion

To avoid interference from removal of halide we chose *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$ and a relatively high concentration of Hg^{2+} (0.2–0.4 *M*). Under these conditions loss of bromide is very fast ($t_{1/2}$ < 5 sec) and this allows the subsequent fate of the immediate reaction product(s) to be studied quantitatively. Two experiments with *cis*-$[Co(en)_2Cl(glyOEt)](ClO_4)_2$ established that following removal of chloride (0.8 *M* Hg^{2+}) this compound behaved in a manner identical with that of the bromo complex.

Rate data for the reaction following removal of bromide are given in Table I (spectrophotometric, 487 nm) and Table II (pmr). The pmr data were obtained by following the growth of the CH_3 resonance of ethanol or the decay of the ester CH_3 signal, Figure 1. All data were collected at 32°, the nmr probe temperature. Also given are rate data for hydrolysis of the chelated ester using separately prepared $[Co(en)_2(glyOEt)](ClO_4)_3$. The method used in making this complex ensures the absence of coordinated water and its purity was verified by its pmr spectrum (acetone-d_6) and by

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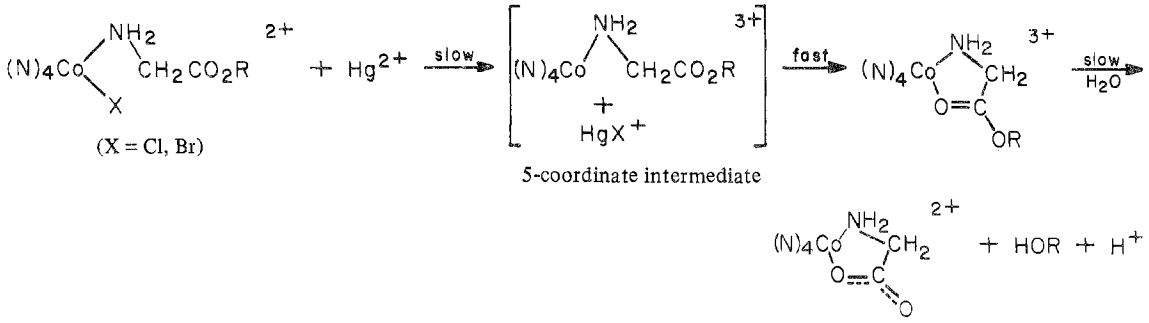
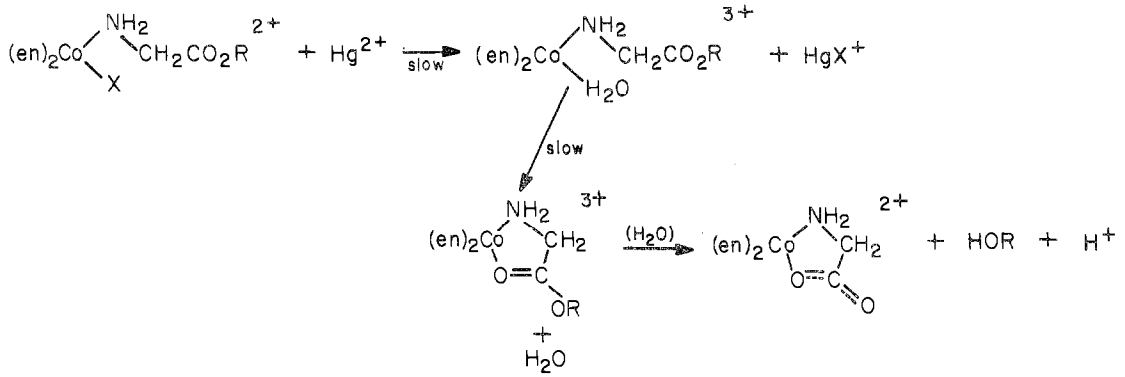
Scheme I



Scheme II



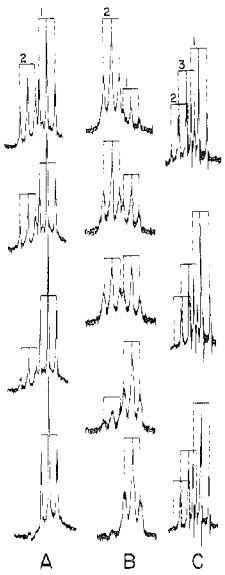


Figure 1. Formation of ethanol (CH_3 triplet 1 centered at 1.10 ppm downfield from NaTPS) following rapid Hg^{2+}-promoted removal of Br^- from *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$ in (A) 0.8 *M* $NaClO_4$ and (B) 3.8 *M* $NaClO_4$. The initial CH_3 triplet at 1.27 ppm (signal 2) is due to the chelated ester. Part C depicts the three CH_3 triplets of ethanol, 1, the chelated ester intermediate, 2, and unreacted starting material, 3, when *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$ was treated with insufficient Hg^{2+} to remove all the coordinated Br^-. Reaction times are as follows from top to bottom: (A) 2.5, 3.5, 4.5, 13 min; (B) 3.5, 8.5, 12, 20, 43 min; (C) 5, 8.5, 10.5 min.

the first-order rate plots which were linear over 4 half-lives. For both complexes linear plots of log $(D_\infty - D_t)$ *vs.* time were obtained (0.08–0.15 OD change) over at least 4 half-lives and clearly only one kinetic process is involved. The final product was verified (pmr, chromatography) to be exclusively the $[Co(en)_2(gly)]^{2+}$ ion.

Figure 1A and B shows changes in the pmr spectra of the CH_3 triplet following treatment of $[Co(en)_2Br(glyOEt)](ClO_4)_2$ (~0.2 *M*) with $Hg(ClO_4)_2$ (0.3 *M*) in 0.1 *M* $DClO_4$ solutions containing 0.8 and 3.8 *M* $NaClO_4$, respectively. Identical spectra and similar rates were obtained when $[Co(en)_2(glyOEt)](ClO_4)_3$ was used. Figure 1C shows the CH_3 region of *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$ when treated with insufficient Hg^{2+} to remove all the coordinated Br^-. The methyl signals of the unreacted starting material, chelated ester, and ethanol are designated.

The following observations can be made.

(1) The observed rates of reaction using both *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$ and $[Co(en)_2(glyOEt)](ClO_4)_3$ agree within experimental error under the same conditions. This suggests, but does not require, that the same process is being followed.

(2) The total optical density increase observed at 487 nm for reaction of the immediate products formed following loss of Br^- from $[Co(en)_2Br(glyOEt)](ClO_4)_2$ (log $(D_\infty - D_t)$ *vs.* time plot extrapolated from $1^1/_3$ min to $t = 0$) is the same (0.085 OD unit, $[HgClO_4] = 0.4$ *M*, 0.2 *M* $HClO_4$, 0.8 *M* $NaClO_4$, $[Co] = 8.9 \times 10^{-4}$ *M*) as that observed for hydrolysis of $[Co(en)_2(glyOEt)](ClO_4)_3$ (8.9×10^{-4} *M*) extrapolated to zero time. This result, together with (1), establishes beyond reasonable doubt that loss of Br^- from *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$ results in exclusive formation of the chelated ester at this ClO_4^- concentration.

(3) A similar total OD change as in (2) (0.089 OD unit) was observed for $[Co(en)_2Br(glyOEt)](ClO_4)_2$ when the reaction was carried out in 3.4 *M* $NaClO_4$, 0.4 *M* $Hg(ClO_4)_2$, and 0.2 *M* $HClO_4$ (extrapolation of log $(D_\infty - D_t)$ *vs.* time plot $1^1/_3$ min after mixing). This, together with (1) and (2), implies that the chelated ester is the exclusive product independent of total $[ClO_4^-]$ at least over the 1.8–4.4 *M* ClO_4^- range.

(4) Increasing the total ClO_4^- concentration from 1.0 to 4.4 *M* *slows* down the rate of the reaction with both *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$ and $[Co(en)_2(glyOEt)](ClO_4)_3$ and by a similar amount, ~3-fold. An even bigger effect on the rate is found in D_2O, ~4-fold. Nomiya and Kobayashi[1] as-

sumed in their kinetic analysis that the rate of hydrolysis of the chelated ester would be independent of $[ClO_4^-]$.

(5) Changing the solvent from H_2O to D_2O slows down hydrolysis for both complexes. At low ClO_4^- (0.8 *M* $NaClO_4$) this reduction is 1.5–2-fold but is more significant (~2.5) in 3.6 *M* $NaClO_4$. Thus the slower rates observed in the pmr experiments result from a solvent effect.

(6) The changes observed in the CH_3 signal derived from *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$ are idenitcal with those observed with $[Co(en)_2(glyOEt)](ClO_4)_3$ under the same conditions. The two sets of signals result from the chelate ester (1.27 ppm) and ethanol (1.10 ppm).

(7) The same CH_3 signals are observed, both initially, during the reaction and, finally, in the absence of added $NaClO_4$ (0.2 *M* $DClO_4$, 0.3 *M* $Hg(ClO_4)_2$, ~0.2 *M* complex) and in 3.6 *M* $NaClO_4$; only the rates of interconversion differ. This confirms that perchlorate does not alter the immediate products following loss of Br^-.

(8) The CH_3 signal of unreacted $[Co(en)_2Br(glyOEt)](ClO_4)_2$ is centered ~6.5 Hz *upfield* from that in the chelated ester and ~11 Hz *downfield* from ethanol. The assignment given by Nomiya and Kobayashi is incorrect.[9] The signal purported by them to result from unreacted $[Co(en)_2Cl(glyOEt)]^{2+}$ (Figure 3A)[1] and $[Co(en)_2(H_2O)(glyOEt)]^{3+}$ (Figure 3B)[1] is in fact due to the chelated ester $[Co(en)_2(glyOEt)]^{3+}$.

The above results demonstrate unequivocally that increasing the ClO_4^- concentration does not alter the mechanism for hydrolysis of the ester function in *cis*-$[Co(en)_2X(glyOEt)]^{2+}$ following treatment with Hg^{2+}; only the rate is altered. Also the data confirm that such hydrolyses proceed exclusively *via* the chelate ester intermediate $[Co(en)_2(glyOEt)]^{3+}$. This is in agreement with our own unpublished observations that aquo ester or aquoamide complexes of the type $[Co(en)_2(OH_2)(glyY)]^{3+}$ (Y = OR, NH_2) hydrolyze rapidly *via* an intramolecular process without formation of $[Co(en)_2(glyY)]^{3+}$ at an intermediate stage.

Registry No. *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$, 49567-52-4; $[Co(en)_2(glyOEt)](ClO_4)_3$, 52613-64-6; ClO_4^-, 14797-73-0.

(9) Comparison of the central peak separations in Figure 3 of Nomiya and Kobayashi[1] suggests that the CH_3 signal of EtOH (Figure 3A) is centered some 10 Hz upfield from the 1.20-ppm signal (which is wrongly assigned); that is at 1.10 ppm rather than at 1.16 ppm. This then agrees with Figure 3B and with our results.

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Metal-Porphyrin Interactions. IV. Electron-Transfer Kinetics between Dithionite and Manganese(III) and Cobalt(III) Porphyrins[1]

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There is much current interest in the mechanisms of electron transfer involving hemoproteins,[2-7] and it is thus surprising that so few studies have been done with the simpler prosthetic group porphyrins[8,9] themselves. To this end, we report the kinetics of reduction (to the divalent state) of a series of cobalt(III) and manganese(III) porphyrins by dithionite ($S_2O_4^{2-}$) in aqueous pyridine solutions. The results show that the kinetic and electrochemical stabilities parallel one another for both metalloporphyrin types. It is argued that the manganese results are consistent with an outer-sphere mechanism.

Experimental Section

The manganese(III) and cobalt(III) porphyrins were prepared by standard methods.[10,11] The dithionite concentration was determined by titration with $Fe(CN)_6^{3-}$, which gave similar results to the Methylene Blue procedure.[9,12] The kinetics were followed in the Soret region using a Durrum–Gibson stopped-flow apparatus. The reactions were run under pseudo-first-order conditions with at least 100-fold excess of total dithionite to total porphyrin (*ca.* 10^{-5} *M*). The first-order rate constant, k_0, was calculated in the usual manner,[13] from triplicate absorbance–time oscilloscope traces. The reactions were done under purified N_2 at 17°, in a distilled pyridine–0.1 *M* NaCl–0.05 *M* Hepes buffer media. Dithionite was analyzed before and after each reaction, and the difference was never more than 2%. This indicates the stability of the reductant under the reaction conditions. No reduction of the macrocycle by dithionite was found except for manganese(III) tetramethyltetrapyridylporphine and manganese(III) diacetyldeuteroporphyrin dimethyl ester. For the former, only ring reduction was found, while with the latter, metal reduction was much faster than ring reduction.

Results

Manganese(III) deuteroporphyrin IX dimethyl ester was the most thoroughly studied compound. In 4 *M* pyridine, the reaction was first order in porphyrin over 3 half-lives, and the observed rate constant, k_0, was independent of total porphyrin from 3×10^{-6} to 17×10^{-6} *M*. The observed rate was independent of pH from 7.4 to 8.1 and half order in total dithionite (see Table I). $k_0/[S_2O_4^{2-}]^{1/2} = 30 \pm 4\ M^{-1/2}$ sec^{-1}. Table I shows that k_0 was fairly independent of pyridine concentration from 2.5 to 4.5 *M* pyridine. Data could not be taken over a greater range due to the insolubility of the porphyrin esters at lower concentrations and of dithionite at higher pyridine concentrations. This small pyridine range certainly limits the mechanistic conclusions that can be drawn, but it is the only way that such data on a wide range of compounds can be obtained. Table II shows the relative rates of reduction of a series of cobalt(III) and manganese(III) porphyrins which differ in their peripheral substituents.

The half-order dependence on dithionite is due to the $S_2O_4^{2-}$–$2SO_2\cdot^-$ equilibria, with the radical anion as the reductant. The equilibrium constant, K_D, has been esti-

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