pentaphenylcyclopentadienyl)dipalladium(I) (4.29×10^{-4} mol) in A.C.S. chloroform (0.75% ethanol added; 99 mL). The solution turned purple and on reducing the volume **16a** was precipitated as a purple solid (58%). Evaporation of the mother liquor to dryness followed by hexane extraction of the residue yielded diphenylacetylene (>90%). Complexes **16b** and **16c** were prepared similarly.

Di-μ-chloro-bis(η^5-pentaphenylcyclopentadienyl)dipalladium(II) (17a). To a solution of complex **1** (0.976 g) in chloroform (50 mL) was added 4.6 mL of a chloroform solution of HCl (0.34 M). The reaction was stirred for 30 min, the solution reduced in volume to 10 mL, n-pentane (70 mL) added, and the solution cooled to 0 °C. The complex **17a** precipitate from the solution as a brown solid (0.761 g; 85%). The complexes **17b** and **17c** were prepared similarly.

The reaction of **17a** with an equimolar quantity of Tl(hfac) in CH_2Cl_2 gave complex **18** as an orange glass (80% yield).

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Reduction Studies on Mixed Chelate Complexes

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Abstract: The Cr^{2+} reductions of the complexes $[Co(en)(ptdn)_2]^+$, $[Co(en)_2(ptdn)]^{2+}$, and $[Co(en)_3]^{3+}$ have been studied. The reaction of $[Co(en)(ptdn)_2]^+$ proceeded by three pathways: inner-sphere monobridged ($k^{25°C} = (2.5 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 13.7 \pm 0.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = -24 \pm 3$ eu), inner-sphere dibridged ($k^{25°C} = (2.1 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 13 \pm 1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -28 \pm 5$ eu), and outer sphere ($k^{25°C} = (2.0 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 10 \pm 2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -36 \pm 7$ eu); $\mu = 1.0$ M (LiClO$_4$). The $[Co(en)_2(ptdn)]^{2+}$ complex was reduced by Cr^{2+} with $k^{50°C} = 5.7 \times 10^{-5}$ M^{-1} s^{-1}, $\mu = 1.0$ M (LiClO$_4$). This reaction was shown to occur partially by an inner-sphere path. For $[Co(en)_3]^{3+}$ only an outer-sphere path is possible and $k^{50°C} = 1.1 \times 10^{-4}$ M^{-1} s^{-1}, $\mu = 1.0$ M (LiClO$_4$). Rate trends within the series $[Co(ptdn)_3]$, $[Co(en)(ptdn)_2]^+$, $[Co(en)_2(ptdn)]^{2+}$, and $[Co(en)_3]^{3+}$ as well as within the analogous oxalato–Co(III) complexes are discussed in terms of ligand field effects.

There do not appear to have been many systematic studies of redox reactions of mixed chelate compounds in which the number of chelate rings of one kind is varied within a series.[1] Such studies are hampered by synthetic difficulties involved in preparing the full series and by problems of solubility in the case of many ligands.

We have recently been interested in the reactions of mixed chelate compounds, particularly those involving pentane-2,4-dionato and derivatives of this ligand.[2] The investigation of rate trends throughout a series of mixed chelates was especially interesting from two points of view. First, the possibility that the changes in rate constants would vary systematically, based on ligand field effects,[3] could be determined, and second, the differences in the detailed mechanism of electron transfer through chelates in general, a rather neglected topic in the study of redox chemistry, could be elucidated.

The series of complexes [Co(ptdn)₃],[4] [Coen(ptdn)₂]⁺, [Coen₂(ptdn)]²⁺, and [Coen₃]³⁺ seemed ideal for an investigation of rate trends in mixed chelates, especially since the Cr^{2+} reduction of the first and last compounds previously had been reported.[5,6] In studying the reaction of Coen(ptdn)₂⁺ with Cr^{2+} we have found evidence for a double-bridged activated complex.[7] This was unexpected since the analogous reaction with Co(ptdn)₃ was shown by Linck and Sullivan[5] to proceed only by the outer-sphere and monobridged inner-sphere paths. Other examples of the transfer of two groups in chelated systems are sparse and involve only the oxalate ligand. Two oxalate ligands have been shown to be transferred in the reaction of Cr^{2+} with $Cr(C_2O_4)_3{}^{3-}$,[8] cis,trans-$Cr(H_2O)_2(C_2O_4)_2{}^-$,[8] and $Co(C_2O_4)_3{}^{3-}$.[9]

We present in this work an extensive study of the reaction of Cr^{2+} with Coen(ptdn)₂⁺, as well as a detailed investigation of rate trends and mechanistic differences throughout the series.

Experimental Section

Reagents. All reagent solutions were prepared in water which was deionized, distilled, and then redistilled from alkaline permanganate in an all-glass apparatus. Lithium perchlorate solutions were made by dissolving anhydrous reagent grade LiClO₄ (G. Frederick Smith Chemical Co.) in water and filtering the resulting solution through a 0.50-μ Millipore filter (Millipore Filter Corp.). Triplicate portions of the filtrate were then standardized by determining the amount of hydrogen ion released from an Amberlite IR-120(H) analytical grade resin (BDH Chemicals Ltd.).

Chromium(II) perchlorate solutions were prepared by reduction of Chromium(III) perchlorate (G. Frederick Smith Chemical Co.) in aqueous perchloric acid solution using zinc–mercury amalgam. The solutions were standardized as reported earlier[10] and were stored and handled using standard syringe technique, in an atmosphere of high-purity argon.

Preparation of Complexes. [Co(en)(ptdn)₂]⁺. The compound was prepared by the method of Archer and Cotsoradis[11] and was purified by ion-exchange on Rexyn(102) in the sodium ion form.[12] The desired purple band was eluted off the column and rotovaped to a concentrated solution, whereupon NaClO₄ (G. Frederick Smith Chemical Co.) was added to precipitate out the complex. Anal. Calcd for [Co(C₂N₂H₈)-(C₅O₂H₇)₂](ClO₄): C, 34.59; H, 5.32; N, 6.72. Found: C, 34.77; H, 5.54; N, 6.69.

[(OH₂)₄Cr(ptdn)]²⁺ and [(OH₂)₂Cr(ptdn)₂]⁺. These complexes were prepared as described previously[2] and were separated by ion exchange on Dowex 50WX8(400) cation-exchange resin at 5 °C.

[(tmed)Co(ptdn)₂]⁺.[13] The compound was prepared by the method of York et al.[14] and was purified in the same manner as the analogous ethylenediamine complex described above. Anal. Calcd for [Co(C₆N₂H₁₆)(C₅O₂H₇)₂](ClO₄): C, 40.64; H, 6.39; N, 5.92. Found: C, 40.01; H, 6.33; N, 6.10.

[Co(en)₂(ptdn)](ClO₄)₂. This compound was prepared as reported in the literature[15] and, after ion exchange on Rexyn(102) in the sodium ion form, the complex was isolated and precipitated with addition of NH₄PF₆. Elemental analysis verified that the resulting product was analytically pure. The sample was then dissolved in triply distilled water and charged back onto a fresh Rexyn column. The red band was physically removed from the column and thoroughly washed with double distilled water while still on the resin, to remove any residual sodium chloride. The complex was librated from the resin using concentrated doubly distilled HClO₄ (G. Frederick Smith Chemical Co.). Solid NaClO₄ was added to the filtered solution which was allowed to sit for 1 month at −5 °C, and the crystals which gradually formed were filtered off.

[Co(en)₃]³⁺. This compound was obtained by a known procedure[16] and was ion-exchanged as described in the previous preparation. The eluting agent was a 0.5 M solution of NaClO₄ made with doubly distilled water. The complex was removed from the resin with double distilled HClO₄ and reagent grade solid NaClO₄ was used to precipitate out the complex directly. Anal. Calcd for [Co(C₂N₂-H₈)₃](ClO₄)₃: C, 13.40; H, 4.50; N, 15.63. Found: C, 13.12; H, 4.69; N, 15.53.

Product Analyses. For the reaction of Cr^{2+} and [Co(en)(ptdn)₂]-(ClO₄), 80–85 μmol of the complex was reacted with an 8–16-fold

Table I. Electronic Spectra of Chromium(III) Products[a]

Complex	λ_{max} (ϵ_{max}), nm (M^{-1} cm^{-1})	Determinations
[(OH₂)₄Cr(ptdn)]²⁺	553 (26.8 ± 0.3)	4
	392 (209 ± 1)	3
	326 (8150 ± 70)	4
	253 (4310 ± 30)	4
[(OH₂)₂Cr(ptdn)₂]⁺	553 (39 ± 3)	4
	388 (358 ± 5)	3
	328 (14000 ± 300)	4
	256 (9200 ± 200)	4

[a] These complexes were made by substitution of pentane-2,4-dione on [Cr(OH₂)₆]³⁺.

excess of Cr^{2+} in 10 mL of a 0.1 M HClO₄ solution. Analyses were also performed on a scale ten times larger than this to check visually for the presence of the chromium(III) inner-sphere products. After the reaction had gone to completion (>5 half-times), the solution was diluted up to about 200 mL and a rapid stream of cleaned air was bubbled vigorously through the solution for 5–10 min to oxidize the excess chromium(II). Chromatographic separation of these reaction mixtures was accomplished on Dowex 50WX8(400) and Dowex 50WX8(200) cation-exchange resins. The eluent obtained upon charging the column and washing it with several column volumes of water was collected and analyzed spectrophotometrically for free ligand. Increasing concentrations of a solution containing NaClO₄ and HClO₄ up to a maximum of 0.5 M NaClO₄ and 0.1 M HClO₄ were used to elute the chromium(III) inner-sphere products. The first band to come off the column was the [(OH₂)₂Cr(ptdn)₂]⁺ complex, followed by the [(OH₂)₄Cr(ptdn)]²⁺ band. A blue solution of [Cr(OH₂)₆]³⁺ was eluted next, leaving at the top of the column the chromium(III) dimer. The last two products were not collected quantitatively.

Product analyses on the reaction of Cr^{2+} with [Co(en)₂(ptdn)]-(PF₆)₂ were carried out at 50 °C in a glass gas scrubber. A constant stream of nitrogen was passed through the solution during the course of the reaction in order to remove any ptdn which might be formed as a result of an outer-sphere path. Reaction mixtures had [Cr^{2+}] = 0.76, [Co(en)₂(ptdn)²⁺] = 0.050, and [H⁺] = 0.20. The reaction time was 24 h and corresponded to approximately 5.5 half-times. Blank experiments were carried out with [Cr^{3+}] = 0.050, [Cr^{2+}] = 0.79, [H⁺] = 0.20, and [ptdn] = 0.050. The ligand was added in exponentially decreasing increments over a period of 18 h and the total reaction time was 24 h. All products were characterized by their UV–visible spectra. Chromium concentrations were determined spectrophotometrically as chromate.

Kinetic Measurements. The rate of reduction of the [Co(en)-(ptdn)₂]⁺ complex was followed by observing the change in absorbance at 490 nm. Similarly, the reactions of Cr^{2+} with [Co(en)₃]³⁺, [Co(en)₂(ptdn)]²⁺, and [(tmed)Co(ptdn)₂]⁺ were monitored at 465, 499, and 556 nm, respectively. The kinetic runs were performed on a Beckman Acta CIII spectrophotometer with the temperature controls described previously.[17] All reactions were carried out in cylindrical cells sealed with rubber serum caps in the absence of oxygen. The reactions were run under pseudo-first-order conditions (reductant in a 20–80-fold excess over oxidant).

Physical Measurements. The ultraviolet and visible spectra were measured on a Beckman Acta CIII spectrophotometer. The proton magnetic resonance spectra were recorded on a Bruker T60 FT spectrometer.

Results

Product Analyses. A preliminary large-scale product analysis at ambient temperature was performed by reacting 814 μmol of [Co(en)(ptdn)₂]⁺ with 6700 μmol of Cr^{2+} in 100 mL of a 0.1 M HClO₄ solution for 8 h. The mixture was then ion exchanged and two purple bands, one of which moved as a 1+ ion and the other of which eluted as a 2+ ion, were clearly observed on the column. The electronic spectra obtained for the 1+ and 2+ ions were identical with those obtained for the complexes [(OH₂)₂Cr(ptdn)₂]⁺ and [(OH₂)₄Cr(ptdn)]²⁺,

Table II. Product Analysis Data for the Cr^{2+} Reduction of $[Co(en)(ptdn)_2]^+$

Temp,[a] °C	Reaction time (h)	Cr^{2+}, μmol used	$[Co(en)(ptdn)_2]^+$, μmol used	$[(OH_2)_4Cr(ptdn)]^{2+}$, μmol recovered	$[(OH_2)_2Cr(ptdn)_2]^+$, μmol recovered	% Mono[b] path	% Di[c] path
25.0	8	671	83.8	31.9	25.4	38.1	30.3
	10	671	85.2	33.4	25.7	39.2	20.2
	12	671	85.2	32.8	28.7	38.5	33.6
					Av	38 ± 1	31 ± 2
35.0	2	671	84.5	34.5	26.8	40.8	31.7
	4	671	86.4	34.9	27.6	40.4	31.9
					Av	40 ± 1	32 ± 1
45.0	1	6710	832	375	258	45.1	31.0
	2	675	83.0	36.5	24.5	44.0	29.5
	4	675	85.5	34.0	30.4	39.8	35.5
					Av	43 ± 3	32 ± 4

[a] The temperature was accurate to within ±1.0 °C. [b] This is the percentage of the reaction which proceeded to give the monosubstituted complex based on moles of $[(OH_2)_4Cr(ptdn)]^{2+}$ recovered per mole of $[Co(en)(ptdn)_2]^+$ used. [c] This is the percentage of the reaction which proceeded to give the disubstituted complex based on moles of $[(OH_2)_2Cr(ptdn)_2]^+$ recovered per mole of $[Co(en)(ptdn)_2]^+$ used.

Table III. Kinetic Data for the Reduction of Bis(pentane-2,4-dionato)ethylenediaminecobalt(III) by Chromium(II)[a]

Temp,[c] °C	$[H^+]$[b]	$10^3 [Co(en)(ptdn)_2]^+$ [b]	$10^2 [Cr]^{2+}$ [b]	$10^2 k_2$, $M^{-1} s^{-1}$
25.0	0.10	1.61	1.52	0.656
	0.10	1.61	1.52	0.656
	0.10	1.74	2.63	0.643
	0.10	2.07	10.4	0.640
	0.20	1.46	5.17	0.631
	0.20	1.46	10.3	0.632
	0.50	1.60	5.17	0.658
	0.70	1.60	5.17	0.627
		$k_2^{25.0} = (6.4 \pm 0.2) \times 10^{-3}$		
35.0	0.10	1.33	10.3	1.45
	0.40	1.34	7.60	1.34
	0.40	1.50	7.90	1.39
	0.40	1.33	10.5	1.35
	0.80	1.09	4.05	1.49
		$k_2^{35.0} = (1.40 \pm 0.09) \times 10^{-2}$		
45.0	0.10	1.33	10.2	2.66
	0.70	1.37	2.95	2.64
	0.70	1.33	2.99	2.61
	0.70	1.37	5.09	2.59
		$k_2^{45.0} = (2.62 \pm 0.04) \times 10^{-2}$		

[a] For all runs, ionic strength $\mu = 1.0$ M (LiClO$_4$). [b] Concentrations are initial values in molar units. [c] The temperature was accurate to ±0.1 °C.

Table IV. Summary of Rate Constants and Activation Parameters for the Chromium(II) Reduction of $[Co(en)(ptdn)_2]^+$

Product	$k^{25°C}$, $M^{-1} s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
Monosubstituted	$(2.5 \pm 0.2) \times 10^{-3}$	13.7 ± 0.9	-24 ± 3
Disubstituted	$(2.1 \pm 0.2) \times 10^{-3}$	13 ± 1	-28 ± 5
$Cr(OH_2)_6^{3+}$	$(2.0 \pm 0.2) \times 10^{-3}$	10 ± 2	-36 ± 7

respectively (see Table I). The 1+ ion accounted for 29% of the total chromium products and the 2+ ion accounted for 34%. The remaining chromium(III) was the parent ion, $[Cr(OH_2)_6]^{3+}$. Similar results were obtained at 45 °C (see Table II).

In the smaller analyses, only the band for the $[(OH_2)_4Cr(ptdn)]^{2+}$ complex could be seen on the column since the $[(OH_2)_2Cr(ptdn)_2]^+$ species was too diffuse. However, those bands containing the disubstituted product were collected by elution with a solution containing 0.03 M NaClO$_4$ and 0.006 M HClO$_4$, and the amount present was determined by running the ultraviolet spectrum of a sample of the eluent.

Because the reaction of Cr^{2+} with $[Co(en)(ptdn)_2]^+$ is slow the possibility exists that the observed products of reduction were formed by substitution reactions after electron transfer. Substitution experiments were carried out where conditions were similar to those in the reduction studies. Reaction mixtures contained $[Cr(OH_2)_6]^{3+}$ (an amount equal to the concentration of $[Co(en)(ptdn)_2]^+$ used in the reduction product
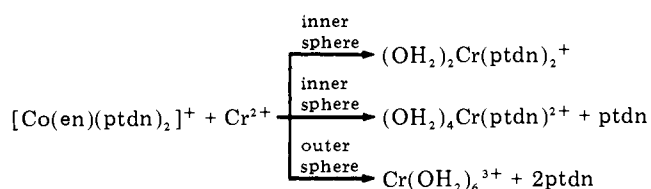
analyses), twice the amount of ptdn, and Cr(II) (the same excess present in the reduction product analyses). For the longest reaction time in Table II at 25 °C, $(8.2 \pm 0.7)\%$ $[(OH_2)_4Cr(ptdn)]^{2+}$ and $(0.2 \pm 0.5)\%$ $[(OH_2)_2Cr(ptdn)_2]^+$ were obtained (compare 38 and 31%, respectively from the electron-transfer studies). At 45 °C, substitution gave $(16 \pm 3)\%$ $[(OH_2)_4Cr(ptdn)]^{2+}$ and $(0.4 \pm 0.2)\%$ $[(OH_2)_2Cr(ptdn)_2]^+$. In addition, similar studies starting with $[(OH_2)_4Cr(ptdn)]^{2+}$ instead of $[Cr(OH_2)_6]^{3+}$ yielded $(2 \pm 1)\%$ of $[(OH_2)_2Cr(ptdn)_2]^+$ at 25 °C and $(1.1 \pm 0.4)\%$ at 45 °C.

For the Cr(II) reduction of $[Co(en)_2(ptdn)]^{2+}$ at 50.0 °C, 47% $[(OH_2)_4Cr(ptdn)]^{2+}$ was isolated and the remaining chromium(III) product was $[Cr(OH_2)_6]^{3+}$. Blank substitution studies under similar conditions gave 34% $[(OH_2)_4Cr(ptdn)]^{2+}$.

Kinetic Results. Kinetic data for the Cr(II) reduction of bis(pentane-2,4-dionato)ethylendiaminecobalt(III) are given in Table III. Contributions from each pathway were evaluated and are summarized in Table IV. No correction was made for symmetry since it cannot be determined whether all oxygens are equivalent or not.

Discussion

The Cr^{2+} reduction of $[Co(en)(ptdn)_2]^+$ was found to proceed with the transfer of one, two, and no ptdn groups. These results can be reasonably interpreted on the basis of the three parallel paths shown below. The inner-sphere path re-

$$[Co(en)(ptdn)_2]^+ + Cr^{2+} \begin{cases} \xrightarrow{\text{inner sphere}} (OH_2)_2Cr(ptdn)_2^+ \\ \xrightarrow{\text{inner sphere}} (OH_2)_4Cr(ptdn)^{2+} + ptdn \\ \xrightarrow{\text{outer sphere}} Cr(OH_2)_6^{3+} + 2ptdn \end{cases}$$

sulting in the transfer of one ptdn ring may proceed by attack of Cr^{2+} on one of the coordinated oxygens of the ptdn ligand

Table V. Rate Constants for Reduction of Selected Chelate Complexes

Oxidant	Reductant	Temp, °C	k_{obsd}, M^{-1} s^{-1}	k_{inner}, M^{-1} s^{-1}	k_{outer}, M^{-1} s^{-1}	λ_{max},[m] nm	Ref
Co(ptdn)$_3$	Cr(II)	50.0	2.85×10^1 [a,k]	1.45×10^1 [k]	1.40×10^1 [k]	591	5
Co(en)(ptdn)$_2{}^+$	Cr(II)	50.0	3.6×10^{-2} [b,j]	1.6×10^{-2} [l] (mono)	8.4×10^{-3} [l]	535	This work
				1.2×10^{-2} [l] (di)			This work
Co(en)$_2$(ptdn)$^{2+}$	Cr(II)	50.0	5.7×10^{-5} [b,g,i,j]	5.7×10^{-5} (?)		499	This work
Co(en)$_3{}^{3+}$	Cr(II)	50.0	1.1×10^{-4} [b,f,h,j]		1.1×10^{-4}	465	This work
		25	3.4×10^{-4}				6
		25	2×10^{-5} [c]				26
(tmed)Co(ptdn)$_2{}^+$	Cr(II)	25	5.8×10^{-4} [b,f,j]				This work
Co(ox)$_3{}^{3-}$	Fe(II)	25	1.1×10^1 [d,n]	1.1×10^1		600	23
Co(en)(ox)$_2{}^-$	Fe(II)	25	1.6×10^{-3} [b,o]	1.6×10^{-3}		544	24
Co(en)$_2$(ox)$^+$	Fe(II)	25	2.28×10^{-5} [e]	2.28×10^{-5}		500	1
Co(en)$_3{}^{3+}$	Fe(II)	25	$<4 \times 10^{-6}$ [b]		$<4.1 \times 10^{-6}$	465	This work

[a] $\mu = 1.0$ M (NaClO$_4$). [b] $\mu = 1.0$ M (LiClO$_4$). [c] $\mu = 0.4$ M (LiClO$_4$). [d] $\mu = 1.0$ M. [e] $\mu = 1.5$ M (H$_2$SO$_4$). [f] 0.2 M HClO$_4$. [g] 0.1–0.2 M HClO$_4$. [h] As PF$_6{}^-$ and ClO$_4{}^-$ salts. [i] As ClO$_4{}^-$ salt. [j] Error limits on the temperature are ±0.5 °C. [k] The values at 50.0 °C were extrapolated from temperature dependence studies at 0.1 M HClO$_4$, R. J. Balahura and J. L. Laird, unpublished results. [l] The value at 50.0 °C was extrapolated from temperature dependence data reported in this work. [m] Position of lowest energy d–d transition. [n] This rate constant is symmetry corrected by a factor of 3. [o] This rate constant is symmetry corrected by a factor of 2.

to give the monodentate product initially. This intermediate can then undergo rapid ring closure by nucleophilic attack of a coordinated water molecule on the free keto carbon to give the final product. This is shown in Scheme I. Such a ring closure reaction has been established by Sargeson et al.[18] for substitution of pentane-2,4-dione on cis-[Co(en)$_2$(OH$_2$)-(OH)]$^{2+}$. The observed product could also be formed if Cr^{2+} attacks two oxygens of the same ring simultaneously. The latter possibility may be sterically less favorable than the mechanism shown in Scheme I.

The formation of the disubstituted complex [(OH$_2$)$_2$-Co(ptdn)$_2$]$^+$ could result from attack of Cr^{2+} at two oxygen atoms of different chelate rings as shown in Scheme II. The initial product, containing two monodentate pentane-2,4-dione ligands, then undergoes ring closure by the same mechanism discussed previously to produce the disubstituted product.

Both Schemes I and II require that the transfer of ligands occurs as a consequence of electron transfer, and thus it is critical to eliminate the possibility that these products result from substitution after electron transfer. Four substitution mechanisms might be envisaged: (1) the reaction goes completely by an outer-sphere path and both of the substituted products arise from substitution of free ligand on Cr(OH$_2$)$_6{}^{3+}$ after the act of electron transfer, (2) the reaction goes partly by an outer-sphere path and partly by a monobridged inner-sphere path with the disubstituted product arising from substitution of free ligand on [(OH$_2$)$_4$Cr(ptdn)]$^{2+}$, (3) either [(OH$_2$)$_4$Cr(ptdn)]$^{2+}$ or [(OH$_2$)$_2$Cr(ptdn)$_2$]$^+$ or both arise from Cr(II) catalyzed substitution of ptdn on a less highly substituted species, and (4) the reaction goes either partially or completely by the dibridged path with [(OH$_2$)$_4$Cr(ptdn)]$^{2+}$ and [(OH$_2$)$_6$Cr]$^{3+}$ resulting from loss of ptdn from a more highly substituted species. Possibility 4 may be readily discounted if ring closure is faster than aquation, since both [(OH$_2$)$_4$Cr(ptdn)]$^{2+}$ and [(OH$_2$)$_2$Cr(ptdn)$_2$]$^+$ are extremely stable once formed, as expected for complexes of the inert Cr(III) ion. No changes may be detected in their UV–visible spectra upon sitting at room temperature for 1 week nor upon storage at 5 °C for several months. If aquation is faster than ring closure the products could result from aquation of the intermediate shown in Scheme II. This possibility cannot be ruled out definitively without labeling studies. However, a mechanism of this type might be expected to give a larger variation in product distribution with temperature than was actually observed. Possibilities 1, 2, and 3 are clearly invalidated by the results of the blank product analyses (see Re-

Scheme I
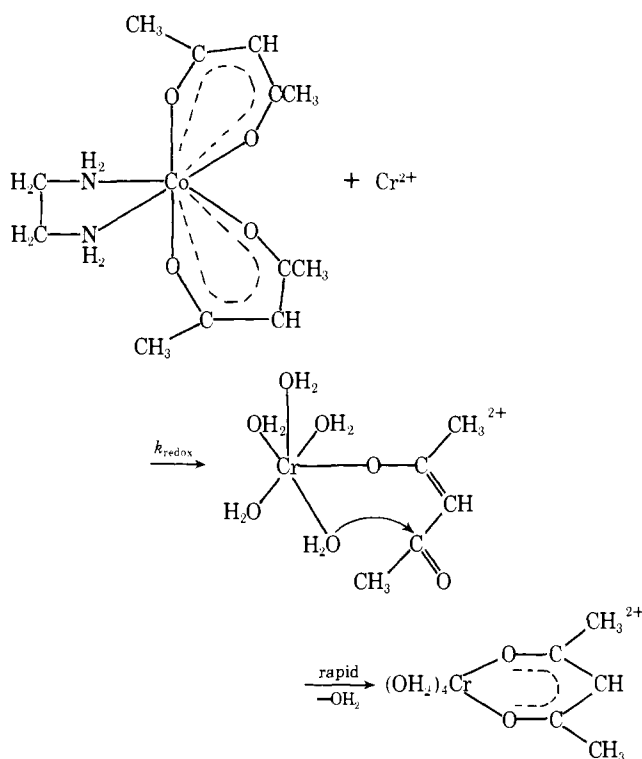
sults). In addition, these substitution mechanisms should yield much more substituted products at higher temperatures than at lower temperatures, but this was not observed.

An inner-sphere path has also been demonstrated in the reduction of Co(ptdn)$_3$ by Cr^{2+}.[5] The inner-sphere path was shown to result in the transfer of one ptdn ring. Surprisingly no disubstituted product was detected. This suggests that the presence of the ethylenediamine ligand may somehow confer a preferred stereochemistry for dibridging on the two ptdn rings of the [Co(en)(ptdn)$_2$]$^+$ complex. Models show that the oxygen atoms opposite the ethylenediamine nitrogens have the proper "bite" size for attack by Cr^{2+} simultaneously on these oxygens. To further investigate this, an attempt was made to reduce the "bite" between the two chelated oxygen atoms opposite nitrogen atoms by replacing the ethylenediamine chelate with N,N,N^1,N^1-tetramethylethylenediamine.

Scheme II
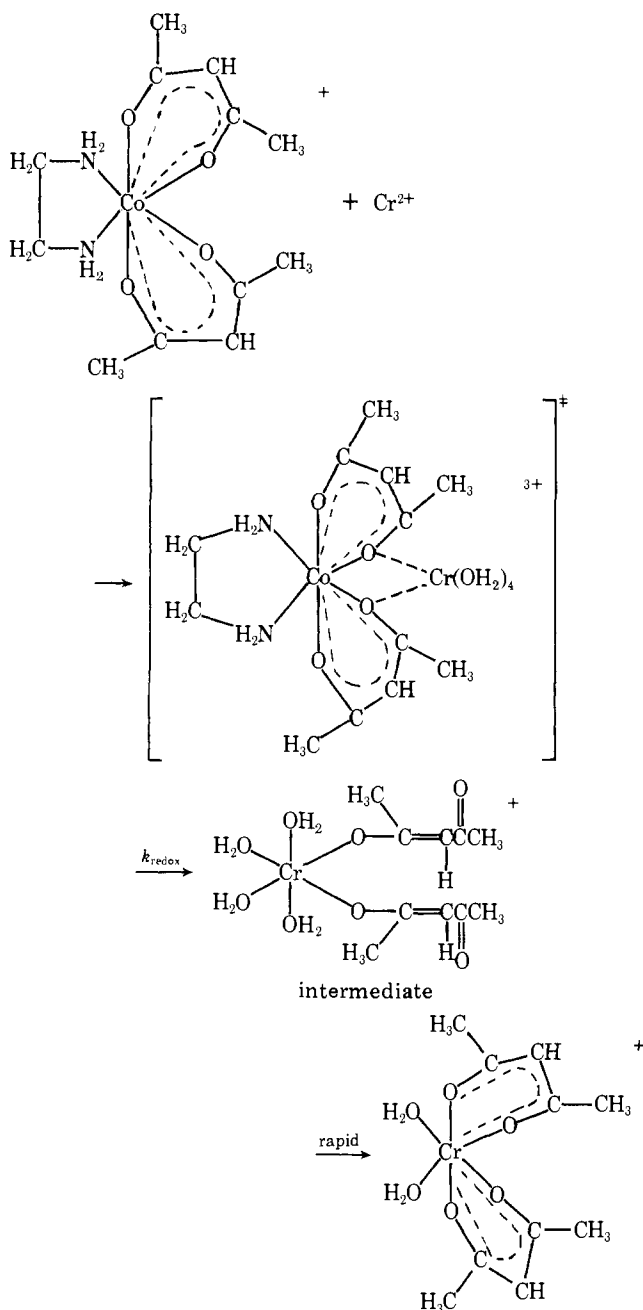
However, [Co(tmed)(ptdn)$_2$]$^+$ was reduced by Cr^{2+} so slowly that it was not possible to determine what paths were being employed.

In the symmetrical Co(ptdn)$_3$ complex rapid conformational changes may occur so that the attacking Cr^{2+} "sees" an average configuration of the ptdn rings resulting in a single-bridged transition state. One type of conformational change available to coordinated ptdn is a loss of pseudoaromatic character due to protonation at the methylene carbon. The formation of the intermediate with a tetrahedral methine
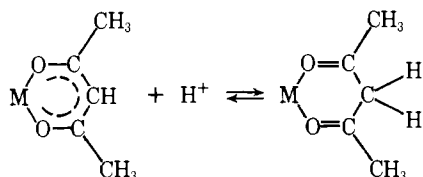
carbon prevents delocalization within the ring. Proton magnetic resonance experiments in acidic D$_2$O show that rapid exchange of the methine hydrogen occurs in Co(ptdn)$_3$ pre-

sumably via protonation at the methine carbon.[19] No exchange is observed for [Co(en)(ptdn)$_2$]$^+$. Thus the rapid interchange between these forms may prevent double bridging in Co(ptdn)$_3$.

A similar nonbridging orienting effect may be responsible for production of a chelated malonate product, Cr-(OH$_2$)$_4$(C$_3$H$_2$O$_4$)$^+$, in the reduction of Co(NH$_3$)$_4$(C$_3$H$_2$O$_4$)$^+$ by chromium(II),[20] whereas a monodentate malonate complex, Cr(OH$_2$)$_5$(C$_3$H$_3$O$_4$)$^{2+}$, is the major product in the reduction of Co(trien)(C$_3$H$_2$O$_4$)$^+$ by chromium(II).[21] Furthermore the chromium(II) reduction of Co(C$_3$H$_2$O$_4$)$_3^{3-}$ results in the transfer of only one malonate ligand and except for [H$^+$] = 0.02 the monodentate product is favored over the bidentate product.[20] In all these cases Cr^{2+} attacks the uncoordinated carbonyl oxygens on malonate and the specific orientations of these rings appear to be important in determining whether one or two rings is transferred and whether the product contains a chelated or monodentate malonate. The orientation of the malonate ring(s) has been shown to be affected by the nature of the other ligand[22] and this appears to be reflected in a change in products for the chromium(II) reductions.

It has also been found that the reaction of Cr^{2+} with Co(C$_2$O$_4$)$_3^{3-}$,[9] Cr(C$_2$O$_4$)$_3^{3-}$,[8] and cis- and trans-Cr-(OH$_2$)$_2$(C$_2$O$_4$)$_2^{-}$[8] results in the transfer of two oxalate ligands. In these systems the 5-membered planar oxalate chelate is much more rigid than in the analogous malonate and ptdn systems and the stereochemistry is more favorable for dibridging.

It appears then that the steric requirements for a doubly bridged transition state for Co(ptdn)$_3$-Cr^{2+} and Co-(C$_3$H$_2$O$_4$)$_3^{3-}$-Cr^{2+} are unfavorable due to rapid conformational interchange.

Trends in the Series. Table V lists the rate constants for reduction of mixed ethylenediamine-pentane-2,4-dione and ethylenediamine-oxalate complexes of cobalt(III). The observed rate constants for the Cr^{2+} reduction of [Co(ptdn)$_3$], [Co(en)(ptdn)$_2$]$^+$, [Co(en)$_2$(ptdn)]$^{2+}$, and [Co(en)$_3$]$^{3+}$ vary approximately as predicted from ligand field arguments[3,5] with the weaker field pentane-2,4-dione ligands conferring a faster rate of reduction than the stronger field ethylenediamine. Quantitatively, the value reported for the Cr^{2+} reduction of [Co(en)$_3$]$^{3+}$ of 3.4 × 10^{-4} M^{-1} s^{-1}[6] at 25 °C is much too fast. A redetermination of this value at 50 °C on a carefully purified sample gave a value of 1.1 × 10^{-4} M^{-1} s^{-1}. This value is still an order of magnitude faster than the reduction rate obtained for [Co(en)$_2$(ptdn)]$^{2+}$.

Considering the separated paths for these reductions a systematic variation in rate constant does occur for [Co(ptdn)$_3$], (Co(en)(ptdn)$_2$]$^+$, and [Co(en)$_2$(ptdn)]$^{2+}$ if it is assumed that the last complex is reduced solely by an inner-sphere process. We could only establish that an inner-sphere path occurs in this system and not to what extent. A plot of log k vs. λ_{max} for the lowest energy d-d transition of each complex gives a straight line. Similarly if the outer-sphere paths are considered for [Co(ptdn)$_3$], [Co(en)(ptdn$_2$]$^+$, and [Co(en)$_3$]$^{3+}$ a similar correlation can also be made.

For the Fe(II) reductions of the ethylenediamineoxalate complexes an inner-sphere mechanism was assumed to operate.[23,24] Again a plot of log k vs. λ_{max} for the lowest energy d-d transition for these complexes is linear. The rates have also been shown to vary linearly with the polarographic half-wave potential for reduction of the oxalate complexes.[25]

Other series of mixed chelate complexes will need to be studied before it can be determined if the energetics of inner- vs. outer-sphere processes can be separated.

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# Stabilities of Trivalent Carbon Species. 3. Reduction of Organic Cations by Chromous Ion[1]

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Abstract: Several organic cations of various structural types are reduced to their corresponding free radicals or dimers by chromous ion in acidic ethanol. Second-order rate constants (L mol^{-1} s^{-1}) for the reductions in 75% ethanol, 2 N HClO$_4$ at 25 °C vary over a range of 10^4: *N*-methylacridinium, 0.02; 2,4,6-triphenylpyrylium, 0.14; sesquixanthylium, 0.6; tropylium, 2.0; flavylium, 10; 9-phenylxanthylium, 110; 9-phenylthioxanthylium, 400. A comparison of chemical reactivity with reduction potential for the organic cations (Marcus treatment) and substituent effects on the reactivity of flavylium ions suggest an outer-sphere activated complex in the electron-transfer reaction. The rate constants for chromous reductions, as log *k*, combined with pK_{R^+} values are used to determine relative stabilities of free radicals. The mechanism of chromous reduction of these cations is compared to reduction of alkyl halides.

Almost all of the information concerning stabilities of trivalent carbon species has been obtained from equilibrium or rate measurements in which these species have been formed from tetravalent precursors. However, the fundamental importance of electron-transfer processes involving organic cations, anions, and radicals has been recognized, and two types of experiments have been useful: measurement of the ionization potentials of free radicals in the gas phase by mass spectrometry and electrochemical measurement of redox potentials in solution. The first method has generally been limited to simpler species, e.g., allyl and benzyl, while the latter method requires species which are reasonably stable, e.g., triphenylmethyl, and there have been few systems amenable to both types of investigation.

In this paper we present the results of a kinetic study of the one-electron reductions of a series of organic cations of various structure by chromous ion. The reductions proceed through an outer-sphere activated complex, and the rate constants are related simply to the equilibrium constants for the electron-transfer reaction.

$$R^+ + Cr^{2+} \rightarrow R\cdot + Cr^{3+} \qquad (1)$$

$$R\cdot \rightleftharpoons 0.5R_2 \qquad (2)$$
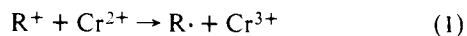
It is possible, therefore, to use relatively simple kinetic measurements to obtain information about the stabilities of free radicals relative to their corresponding cations.

Conant and his co-workers[4] investigated metal ion reductions of organic cations more than 50 years ago and found the principal organic products to be dimers of the first formed radicals or the radicals themselves if they were sufficiently stable. Conant used the reaction in potentiometric titrations, but he did not measure the rates of the redox reactions.

A review of one-electron reductions of organic cations has been published recently.[5]

We reported earlier that in aqueous solution tropylium cation is quantitatively reduced to ditropyl by chromous ion,[6] and Okamoto and his co-workers subsequently studied the reaction in detail.[7] Okamoto also investigated the reduction of tropylium cations with zinc[7a,8] and cyclopropenium cations with chromous ion.[9] In their study of the reduction of tropylium and cyclopropenium cations, Okamoto and co-workers used aqueous hydrochloric acid as solvent. They showed that chloride ion acts as a bridging group in the electron transfer and the rate of reduction by chromous ion increases toward a maximum with increasing chloride concentration. They concluded that in the absence of a bridging anion, a water molecule in the coordination sphere of chromous ion serves as a bridge for the electron transfer.[7c]

We have examined the chromous ion reduction of a series of organic cations of differing structures and reactivity in the absence of bridging anions: *N*-methylacridinium, **1**; 2,4,6-triphenylpyrylium, **2**; sesquixanthylium, **3**; tropylium, **4**; flavylium, **5**; 9-phenylxanthylium, **6**; 9-phenylthioxanthylium, **7**.