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Electron-Transfer Reactions of Optically Active $[Co(phen)_3]^{3+/2+}$ and Derivatives

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The kinetics of the self-exchange reactions of $[Co(phen)_3]^{3+/2+}$, $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$, and $[Co(5,6\text{-}Me_2phen)_3]^{3+/2+}$ (phen = 1,10-phenanthroline) have been examined at 25.0 °C and 0.10 M ionic strength by observing the racemization of the optically enriched oxidized form in the presence of the racemic reduced form. Reaction rates are found to be dependent on the nature of the counterion, and the formation of ion multiplets is proposed. Activation parameters have been determined for the $[Co(phen)_3]^{3+/2+}$ reaction. The kinetics of the oxidation of the complexes $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ and $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ by $[Co(phen)_3]^{3+}$ have also been investigated. They are outer-sphere processes with a simple first-order dependence on both reactants. The oxidation of $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ by $[Co(phen)_3]^{3+}$ is shown to be stereoselective with a 15% ΔΛ stereochemical preference.

Introduction

Thirty years ago, the rate of electron transfer between $[Co(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) and $[Co(phen)_3]^{2+}$ was measured[3] by ^{60}Co exchange at 0 °C. The presently accepted value for this rate constant, calculated to be around 40 M^{-1} s^{-1} at 25 °C, is an extrapolation using activation parameters reported a decade later as a footnote in a paper by Farina and Wilkins.[4] Self-exchange racemization of $[Co(phen)_3]^{3+}$ is an important limitation in chiral induction in electron-transfer reactions examined in one laboratory involved in this study. A need has arisen for more accurate self-exchange rate data at 25 °C. The results reported in this paper are from two independent investigations, one of which employed polarimetry and the other circular dichroism to monitor the reactions. Both are in excellent agreement, which prompted this joint publication.

The specific rate for the $[Co(phen)_3]^{2+}$-catalyzed racemization of $[Co(phen)_3]^{3+}$ is related directly to the self-exchange rate provided it is slower than the rate of racemization[5] of the labile $[Co(phen)_3]^{2+}$ (6.9 s^{-1}) and also provided that the electron-transfer process shows no chiral discrimination. While the presence of stereoselectivity in the self-exchange reaction is difficult to determine, observation of this phenomenon in electron-transfer reactions between metal–phenanthroline complexes is of considerable interest. Early experiments reporting[6] chiral induction in $[Cr(phen)_3]^{3+}$ formed from the oxidation of $[Cr(phen)_3]^{2+}$ by $[\Delta\text{-}Co(phen)_3]^{3+}$ promoted a great deal of theoretical[7] and experimental[8] interest in electron-transfer stereoselectivity but were subsequently shown to be in error.[8] Although it has been pointed out[9] that the absence of stereoselectivity in these reactions is due to experimental difficulties rather than any intrinsic lack of stereoselectivity in electron transfer between metal–phenanthroline complexes, this fact has not been fully appreciated.

In this paper the self-exchange rate for the $[Co(phen)_3]^{3+/2+}$ system has been determined directly at 25 °C from the rate of racemization of $[\Lambda\text{-}(+)_{589}\text{-}Co(phen)_3]^{3+}$ in the presence of $[Co(phen)_3]^{2+}$. Anion effects and activation parameters have also been examined. The corresponding self-exchange rates for the methylated derivatives $[Co(4,7\text{-}Me_2phen)_3]^{3+,2+}$ and $[Co(5,6\text{-}Me_2phen)_3]^{3+,2+}$, which are poorly defined in the literature,[10-12] have also been evaluated directly. Stereoselectivity has been investigated in cross-reactions between these metal–phenanthroline derivatives.

Experimental Section

(a) **Materials.** The synthesis of $[\Lambda\text{-}(+)_{589}\text{-}Co(phen)_3](ClO_4)_3\cdot 2H_2O$ has been described previously.[3,13] Racemic $[Co(phen)_3](ClO_4)_3\cdot 2H_2O$ was prepared by the addition of 6 mL of 30% hydrogen peroxide to $CoCl_2\cdot 6H_2O$ (0.72 g, 3 mmol), 1,10-phenanthroline monohydrate (Fluka) (1.80 g, 9 mmol), and 6 mL of concentrated HCl in 150 mL of water. The solution was evaporated at 80 °C to about 15 mL, and a further 300 mL of water was added. On addition of 3 mL of 72% perchloric acid the product precipitated as a yellow powder and was collected by filtration. The crude product was recrystallized from 100 mL of hot water containing 2 mL of 30% hydrogen peroxide and a few drops of perchloric acid to give brown crystals of $[Co(phen)_3](ClO_4)_3\cdot 2H_2O$ (yield 82%). The corresponding chloride salt, $[Co(phen)_3]Cl_3\cdot 7H_2O$, was obtained by absorption of the complex ion on a 70 mm × 5 mm diameter Sephadex-SP C-25 ion-exchange column, washing with water and 0.1 M HCl, and elution with 0.5 M HCl followed by evaporation to dryness under reduced pressure at 40 °C. For some experiments, solutions of the complex with a desired anion were obtained by stirring a suspension of the perchlorate salt with Dowex 1-X8 anion-exchange resin in the appropriate form until exchange was accomplished and removing the resin by filtration. The strong affinity of the resin for perchlorate ion is the basis for this convenient conversion.

$[Co(4,7\text{-}Me_2phen)_3](ClO_4)_3\cdot 2H_2O$ and $[Co(5,6\text{-}Me_2phen)_3](ClO_4)_3$ were prepared by the addition, under argon, of the recrystallized free ligand (0.748 g, 3.3 mmol) in the minimum quantity of ethanol (<30 mL) to $CoCl_2\cdot 6H_2O$ (0.250 g, 1.05 mmol) in 25 mL of water. After the addition of 22 mL of bromine water, the solution was refluxed for 48 h in the dark under argon, and further small quantities of bromine water were added periodically. The products were obtained on addition of 20 mL of 72% perchloric acid to the hot solution. Partial resolution of both complexes was achieved on a 500 mm × 15 mm diameter Sephadex-SP C-25 column eluted with 0.1 M potassium (+)-antimonyl tartrate (Fluka). The optically enriched fractions obtained from this column were converted to the chloride salt by ion-exchange on a 70 mm × 5 mm diameter Sephadex-SP C-25 column as described above. The chloride salts are multiple hydrates, and the extent of hydration is variable, but analyses are in reasonable agreement with the published compositions.[14] An alternative partial resolution involved the addition of potassium (+)-tris[L-cysteinesulfinato(2−)-*SN*]cobaltate(III)[15] (0.09 g, 0.12 mmol) in the minimum volume of water to a solution containing $[Co(4,7\text{-}Me_2phen)_3]Cl_3$ or $[Co(5,6\text{-}Me_2phen)_3]Cl_3$ (0.23 g, 0.24 mmol). The resulting precipitate contained the $(+)_{589}$ salt enriched in both cases, and this was converted to the chloride salt by ion-exchange chromatography.

The ligands 1,10-phenanthroline monohydrate (phen, Fluka) and 2,2′:6′,2″-terpyridine (terpy, Sigma) were used as received. The ligands 4,7-dimethyl-1,10-phenanthroline monohydrate (4,7-Me_2phen, G. F. Smith) and 5,6-dimethyl-1,10-phenanthroline monohydrate (5,6-Me_2phen, G. F. Smith) were recrystallized (typically three times) from hot 1:1 water–ethanol solution to give white needles. Solutions of the

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Table I. Spectroscopic Data for the Complexes $[(+)_{589}\text{-Co}(4,7\text{-Me}_2\text{phen})_3]^{3+}$ and $[(+)_{589}\text{-Co}(5,6\text{-Me}_2\text{phen})_3]^{3+}$ in Aqueous Solution at 25.0 °C

complex	absorption λ, nm	 ε, $M^{-1}\,cm^{-1}$	circular dichroism[a] λ, nm	 Δε, $M^{-1}\,cm^{-1}$
$[(+)_{589}\text{-Co}(4,7\text{-Me}_2\text{phen})_3]^{3+}$			478	0.13
	349	5.2×10^3	346	0.43
	332	5.6×10^3	332	0.71
	274	8.7×10^4	283	24.6
	219	1.13×10^5	270	-15.8
	205	1.01×10^5	229	13.7
$[(+)_{589}\text{-Co}(5,6\text{-Me}_2\text{phen})_3]^{3+}$			480	0.36
	362	5.0×10^3	296	50.8
	286	6.8×10^4	282	-62.9
	247	8.5×10^4	250	12.2
	218	1.12×10^5	228	63.3

[a] Circular dichroism data correspond to the greatest optical purity obtained.

cobalt(II) complexes were prepared from $Co(NO_3)_2 \cdot 6H_2O$ (Baker, Analyzed), $CoBr_2 \cdot 6H_2O$, and $CoCl_2 \cdot 6H_2O$, with a sufficient excess of the appropriate ligand to ensure >99% formation of the tris complex in accordance with known stability and acidity constants.[16] Cobalt(II) ion concentrations were determined spectrophotometrically before the addition of the free ligand ($[Co(H_2O)_6]^{2+}$, $\epsilon = 4.84\ M^{-1}\,cm^{-1}$ at 512 nm).[17] Solutions of the $[Co(4,7\text{-Me}_2\text{phen})_3]^{2+}$ complex and, to a lesser extent, those of the $[Co(5,6\text{-Me}_2\text{phen})_3]^{2+}$ complex are sensitive to autoxidation,[12] and hence these solutions were prepared and used under an atmosphere of argon gas. All solutions were prepared immediately before use. The methylated cobalt(II) salts have limited solubility in nitrate media, and in some instances solutions, cooled slowly to 25 °C from higher temperatures but supersaturated, were used before the onset of precipitation was detected spectrophotometrically.

(b) Methods. Self-exchange rates were measured by observing the decay of the optical rotatory dispersion signal at 589 nm or the circular dichroism signal, ϕ, at 487 nm for $[\Lambda\text{-}(+)_{589}\text{-Co(phen)}_3]^{3+}$, 478 nm for $[\Lambda\text{-}(+)_{589}\text{-Co}(4,7\text{-Me}_2\text{phen})_3]^{3+}$, and 480 nm for $[\Lambda\text{-}(+)_{589}\text{-Co}(5,6\text{-Me}_2\text{phen})_3]^{3+}$. For the self-exchange reactions, the cobalt(III) concentrations varied from 7.5×10^{-5} to 10^{-2} M and the cobalt(II) concentrations varied from 1×10^{-4} to 2.5×10^{-3} M. The reactions are first-order in cobalt(III) concentration over this range of conditions. Plots of $\ln(\phi - \phi_\infty)$ were generally linear for at least 3 half-lives, and pseudo-first-order rate constants, k_{obsd}, were calculated from the slopes by least-squares analysis. The pseudo-first-order rate constants are collected in Tables SI and SII, available as supplementary material.

The rates of reduction of $[Co(phen)_3]^{3+}$ by $[Co(4,7\text{-Me}_2\text{phen})_3]^{2+}$ and $[Co(5,6\text{-Me}_2\text{phen})_3]^{2+}$ were measured in an analogous fashion but under pseudo-first-order conditions with an excess of the reductant. Stereoselectivity in the reduction by $[Co(4,7\text{-Me}_2\text{phen})_3]^{2+}$ was determined by monitoring the circular dichroism signal from the product, $[Co(4,7\text{-Me}_2\text{phen})_3]^{3+}$, produced in reaction with $[\Lambda\text{-}(+)_{589}\text{-Co(phen)}_3]^{3+}$ at 448 nm, where the signal from $[\Lambda\text{-}(+)_{589}\text{-Co(phen)}_3]^{3+}$ is zero, and at 480 nm, near the maximum of the $[Co(4,7\text{-Me}_2\text{phen})_3]^{3+}$ complex. This signal decays as a result of self-exchange racemization.

Circular dichroism measurements were made on an Aviv Model 60DS circular dichroism spectropolarimeter at 25.0 ± 0.2 °C. Polarimetry measurements were made with use of a Bendix-Ericsson recording polarimeter incorporating a water-jacketed Pyrex glass cell with a 4.93-cm path length. Temperature control of the cell was better than ±0.1 °C. UV-visible spectra were recorded on a Varian DMS-100 spectrophotometer. NMR spectra were run on a Nicolet NT 300-MHz instrument.

Results and Discussion

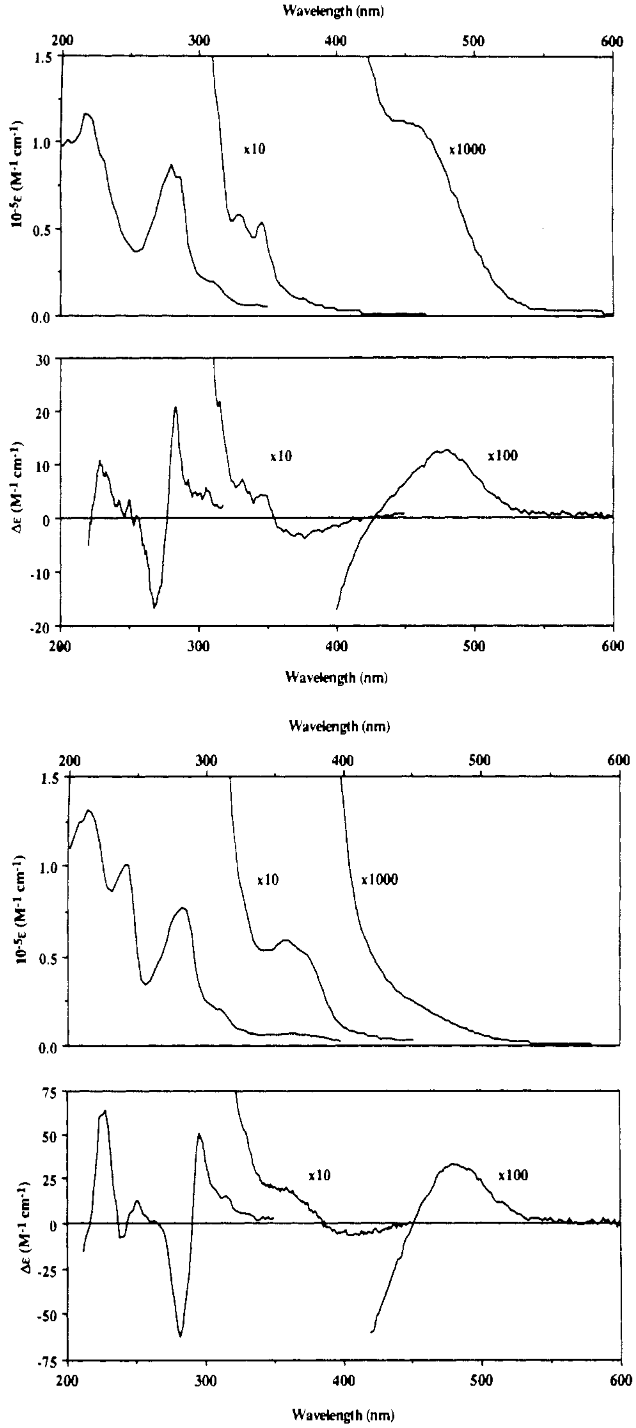

Figure 1. Absorption and circular dichroism spectra of the complexes (a, top) $[\Lambda\text{-}(+)_{589}\text{-Co}(4,7\text{-Me}_2\text{phen})_3]^{3+}$ and (b, bottom) $[\Lambda\text{-}(+)_{589}\text{-Co}(5,6\text{-Me}_2\text{phen})_3]^{3+}$ at 25.0 °C.

(a) Resolution and Characterization of the Complexes. The cobalt(III) complexes $[Co(phen)_3]^{3+}$, $[Co(4,7\text{-Me}_2\text{phen})_3]^{3+}$, and $[Co(5,6\text{-Me}_2\text{phen})_3]^{3+}$ are substitution inert and can be optically resolved. The procedure for preparation of $[\Lambda\text{-}(+)_{589}\text{-Co(phen)}_3]^{3+}$ involves chlorine oxidation of the antimonyl tartrate salt of the corresponding labile cobalt(II) form.[13] However, this fails when the methyl-substituted derivatives are used. Alternative resolving strategies were attempted for these cobalt(III) derivatives. Some success attended the use of tris[L-cysteinesulfinato(2−)-*SN*]cobaltate(III) as a resolving agent for the cobalt(III) complexes. However, the most successful procedure involved elution of the cobalt(III) complex with 0.1 M antimonyl tartrate on a Sephadex cation-exchange column. Characteristics of the first eluted isomers are given in Table I, where comparisons[18,19] of the spectroscopic extrema with those of $[\Lambda\text{-}(+)_{589}\text{-Co(phen)}_3]^{3+}$ suggest assignment of the absolute configuration Λ for both $[(+)_{589}\text{-Co}(4,7\text{-Me}_2\text{phen})_3]^{3+}$ and $[(+)_{589}\text{-Co}(5,6\text{-Me}_2\text{phen})_3]^{3+}$. These complexes were not obtained in a reproducibly optically pure form,[20] and

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Table II. Stepwise Stability and Acidity Constants for Cobalt(II) Complexes with 1,10-Phenanthroline and Its Substituted Derivatives and Reduction Potential Data for the Cobalt(III) Complexes, at 25.0 °C and 0.10 M Ionic Strength[16,21]

ligand	$\log K_1$	$\log K_2$	$\log K_3$	pK_{a1}	$E°$, mV
phen	6.96	6.73	6.08	4.98	355
4,7-Me_2phen	8.08	8.00	8.43	5.95	160
5,6-Me_2phen	7.47	8.00	8.14	5.60	230

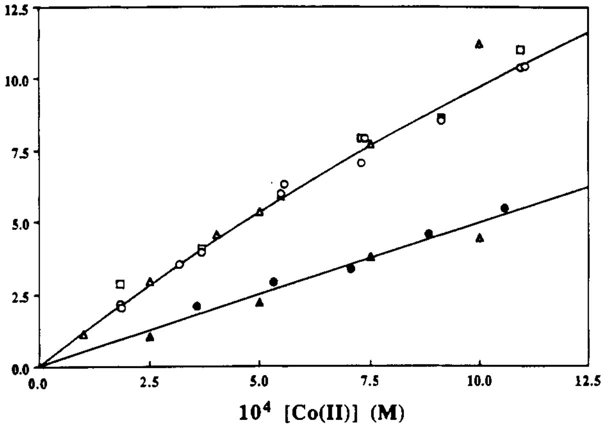

Figure 2. Plot of pseudo-first-order rate constant versus $[Co(phen)_3]^{2+}$ concentration at 25.0 ± 0.2 °C in (i) 0.10 M nitrate media, pH = 6.4, 0.01 M acetate buffer (open circles), (ii) 0.10 M nitrate media, pH = 7.0, 0.01 M Trizma buffer (open squares), (iii) 0.10 M nitrate media, pH ≈ 6.0, unbuffered (open triangles), (iv) 0.10 M chloride media, pH = 6.4, 0.01 M acetate buffer (closed circles), and (v) 0.10 M chloride media, pH ≈ 6.0, unbuffered (closed triangles). Data sets i, ii, and iv were obtained by circular dichroism measurements and sets iii and v by polarimetry.

the optical purity was approximated by comparison with the characteristics of the parent $[\Lambda\text{-}(+)_{589}\text{-}Co(phen)_3]^{3+}$. Absorption and circular dichroism spectra of the $[(+)_{589}\text{-}Co(4,7\text{-}Me_2phen)_3]^{3+}$ and $[(+)_{589}\text{-}Co(5,6\text{-}Me_2phen)_3]^{3+}$ species are shown in Figure 1a,b, respectively.

While the cobalt(III) complexes can be isolated as discrete inert species, the corresponding cobalt(II) complexes are substitution labile and were prepared in solution with sufficient excess of the free ligand to ensure quantitative formation of the tris complex in accord with the stability constant data of Table II. The cobalt(II) complexes have very limited solubility in nitrate, triflate, and perchlorate media, and this restricts the concentration ranges available for kinetic studies. The reduction potentials of $[Co(phen)_3]^{3+}$, $[Co(4,7\text{-}Me_2phen)_3]^{3+}$, and $[Co(5,6\text{-}Me_2phen)_3]^{3+}$, determined[21] by cyclic voltammetry on solutions of the cobalt(II) complexes in nitrate media at 0.10 M ionic strength and 25.0 °C, are also presented in Table II.

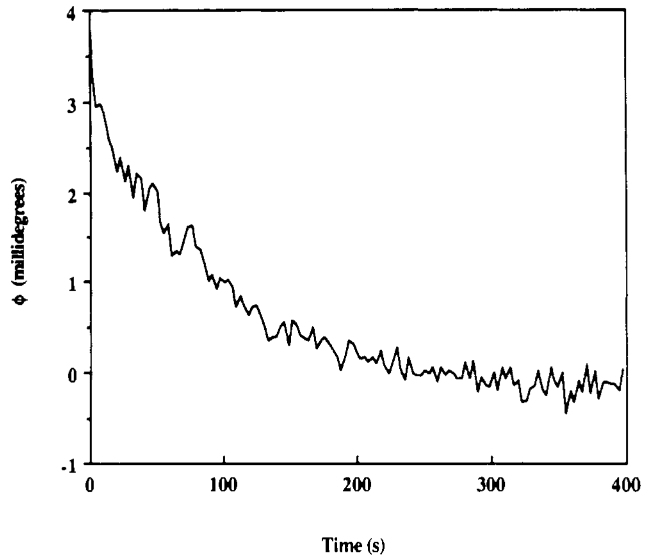

Figure 3. Decay of the circular dichroism signal (φ, mdeg) at 487 nm for $[\Lambda\text{-}(+)_{589}\text{-}Co(phen)_3]^{3+}$ (8.4×10^{-5} M) in the presence of $[rac\text{-}Co(phen)_3]^{2+}$ (1.1×10^{-3} M) in 0.10 M nitrate media at 25.0 °C.

Table III. Second-Order Rate Constants for the Self-Exchange Reaction of $[Co(phen)_3]^{3+/2+}$ at 25.0 °C in the Presence of Various Anions

anion	[anion], M	$k_{\Delta\Lambda}$, M^{-1} s^{-1}	anion	[anion], M	$k_{\Delta\Lambda}$, M^{-1} s^{-1}
NO_3^-	0.008	3.0 ± 0.7	Cl^-	0.006	1.73 ± 0.08
	0.018	3.7 ± 0.3		0.018	2.07 ± 0.12
	0.027	4.7 ± 0.3		0.020	2.00 ± 0.05
	0.10	12.0 ± 0.3		0.10	4.9 ± 0.4
	0.20	16.3 ± 0.8		0.20	8.0 ± 0.3
Cl^-	0.004	1.55 ± 0.11	Br^-	0.10	6.5 ± 0.3
	0.005	1.76 ± 0.05	ClO_4^-	0.006	5.59

(b) Self-Exchange Reactions. In 0.10 M chloride media, the rate law for racemization of $[Co(phen)_3]^{3+}$ is given by eq 1. The

$$-d\phi/dt = \{k_a + k_b[Co(II)]\}\phi \qquad (1)$$

loss of optical activity, φ, in solutions of $[Co(phen)_3]^{3+}$ can be ascribed to two sources: (i) the intrinsic racemization of $[Co(phen)_3]^{3+}$, with $k_a = 2k^{III}_{inv}$, which is independent of the concentration of added $[Co(phen)_3]^{2+}$ (eq 2) and (ii) racemization

$$[\Lambda\text{-}Co(phen)_3]^{3+} \rightleftharpoons [\Delta\text{-}Co(phen)_3]^{3+} \quad k^{III}_{inv} \qquad (2)$$

$$[\Lambda\text{-}Co(phen)_3]^{3+} + [\Delta\text{-}Co(phen)_3]^{2+} \rightleftharpoons [\Lambda\text{-}Co(phen)_3]^{2+} + [\Delta\text{-}Co(phen)_3]^{3+} \quad k_{\Delta\Lambda} \qquad (3)$$

$$[\Lambda\text{-}Co(phen)_3]^{2+} \rightleftharpoons [\Delta\text{-}Co(phen)_3]^{2+} \quad k^{II}_{inv} \qquad (4)$$

by an electronic self-exchange reaction with $[Co(phen)_3]^{2+}$, $k_{\Delta\Lambda}$, driven by the more rapid rate of racemization of the reduced complex (eqs 3 and 4). If the equilibrium in eq 4 is established very rapidly relative to the rate in eq 3, then $k_b = k_{\Delta\Lambda}$ and can be related to the rate of the self-exchange process, k_{11}. A plot of the observed rate constant, k_{obsd}, against [cobalt(II)] is shown in Figure 2. Least-squares analysis of the combined data from both polarimetry and circular dichroism studies gives $k_a = (6 \pm 22) \times 10^{-5}$ s^{-1}, zero within experimental error,[22] and $k_b = 4.9 \pm 0.3$ M^{-1} s^{-1}.

In 0.10 M nitrate media, the decay in the circular dichroism signal is also exponential (Figure 3). For a given cobalt(II) concentration, the specific rate constants are higher, but the data

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(20) The first eluted isomers of the ions $[(+)_{589}\text{-}Co(4,7\text{-}Me_2phen)_3]^{3+}$ and $[(+)_{589}\text{-}Co(5,6\text{-}Me_2phen)_3]^{3+}$ (obtained as the chloride salts) were respectively approximately 10% and 30% optically pure, estimated from comparisons with the parent $[\Lambda\text{-}(+)_{589}\text{-}Co(phen)_3]^{3+}$. Attempts to obtain these complexes as optically pure samples proved difficult, as the extent of resolution appears critically dependent on the presence of trace cobaltous ion or other reducing species. Elution of the Sephadex columns with 5×10^{-4} Na_2H_2edta after absorption of the metal complexes appeared to remove most of these impurities, although the wisdom of this procedure is called into question by our observation that the columns with higher cobaltous ion concentrations produced enhanced resolution. Repeated recrystallization to constant optical activity was ruled out as a practical alternative on the grounds of the high cost of the methylated phenanthroline compounds. Attempts to determine optical purity directly by NMR spectroscopy, using the shift reagent $[Eu(tfc)_3]$ in CD_2Cl_2, failed due to the low solubility of these complexes in methylene chloride (Barton, J. K.; Nowick, J. S. *J. Chem. Soc., Chem. Commun.* **1984**, 1650–1652). In D_2O solution, an excess of the aqueous shift reagent $[Eu(R\text{-}pdta)]^-$ did produce a small upfield shift in the aromatic peaks; however, no enantiomeric discrimination was detected (Kabuto, K.; Sasaki, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 670–671).

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(22) Although it is tempting to ascribe the first-order rate constant, k_a, to intrinsic racemization in $[Co(phen)_3]^{3+}$, it is unwise to do so, since trace amounts of cobalt(II) and reducing impurities in the system promote racemization by the more important self-exchange pathway. In the absence of added $[Co(phen)_3]^{2+}$, racemization of $[Co(phen)_3]^{3+}$ has a half-life in excess of 3 weeks, negligible on the time scale of the cobalt(II)-catalyzed pathway.

can be described by the same rate law with $k_a = (6 \pm 2) \times 10^{-4}$ s^{-1} and $k_b = 9.3 \pm 0.3$ M^{-1} s^{-1}. In this case, the intercept is significant and is much larger than the observed rate of racemization of $[Co(phen)_3]^{3+}$ in the absence of added $[Co(phen)_3]^{2+}$, which is of the order of 10^{-7} s^{-1}. Although deviations from a first-order dependence are small, on the order of 20%, a better fit to the data is achieved with the more complex rate law eq 5, where $k_c = 12.0 \pm 0.3$ M^{-1} s^{-1} and $K_d = 230 \pm 50$ M^{-1}.

$$k_{obsd} = k_c[Co(II)]/\{1 + K_d[Co(II)]\} \qquad (5)$$

Interpretation of this rate law presents some difficulties. A rate-limiting first-order process involving $[Co(phen)_3]^{3+}$ is unlikely, since it has not been detected in other electron-transfer reactions. Medium effects cannot be ruled out. However, precautions have been taken to maintain a medium that is sensibly constant with respect to both anion concentration[23] and also to free phen concentration. In addition, a plausible mechanism for the reaction must explain the rate dependence on anions.

A strong anion dependency was also noted previously[3] for the reaction studied by isotope exchange at 0 °C and was further investigated in this study. Second-order rate constants for the self-exchange rate, obtained in a variety of media of differing ionic composition, are presented in Table III. Even at the lowest concentrations used, specific anion effects are present. Use of standard ionic strength treatments for the data is therefore inappropriate.[24] The accelerating effect on the rate is in the order $ClO_4^- > NO_3^- > Br^- > Cl^-$. It seems plausible that the explanation for the anion dependence lies in the formation of ion pairs, which reduce the electrostatic repulsions between the reactants. Both $[Co(phen)_3]^{3+}$ and $[Co(phen)_3]^{2+}$ are known[25] to associate more strongly with anions in the order $ClO_4^- > I^- > Br^- > Cl^-$. Interestingly, this same order $ClO_4^- > I^- > NO_3^- \approx Br^- > Cl^-$ is observed[26] in the binding of anions to strong-base anion-exchange resins and has been correlated with the solvation properties of the anion, particularly their solvation enthalpies. In the formation of the ion pair, the anions are desolvated, at least partially, and so the anion with the smallest solvation enthalpy will require the least energy for desolvation and will be bound most readily.

The proposed mechanism involves formation of a precursor assembly between the reactants (eqs 6 and 7), which is kinetically important in nitrate media. The apparent association constant

$$[Co(phen)_3]^{3+} + [Co(phen)_3]^{2+} \rightleftharpoons \{[Co(phen)_3]^{3+},[Co(phen)_3]^{2+}\}^* \qquad (6)$$

$$\{[Co(phen)_3]^{3+},[Co(phen)_3]^{2+}\}^* \rightarrow [Co(phen)_3]^{2+} + [Co(phen)_3]^{3+} \qquad (7)$$

in 0.10 M nitrate media, $K = 230$ M^{-1}, is unreasonably large for a process involving two cations, and it is proposed that the species $\{[Co(phen)_3]^{3+},[Co(phen)_3]^{2+}\}^*$ has associated with it an undetermined number of anions. The values for the second-order rate constants at low cobalt(II) concentration, $k_{\Delta\Lambda}$, are 4.9 M^{-1} s^{-1} in 0.10 M chloride media and 12.0 M^{-1} s^{-1} in 0.10 M nitrate media. Rate measurements at a series of temperatures in the range 9–41 °C give the activation parameters $\Delta H^* = 35.3$ kJ mol^{-1}, $\Delta S^* = -113$ J K^{-1} mol^{-1} in 0.10 M chloride and $\Delta H^* = 20.6$ kJ mol^{-1}, $\Delta S^* = -156$ J K^{-1} mol^{-1} in 0.10 M nitrate. These activation parameters are also consistent with formation of a precursor assembly that incorporates one or more anions.

The rate in 0.10 M nitrate solutions evaluated from the present data is a factor of 4 lower than the value of 40 M^{-1} s^{-1} generally accepted for the self-exchange rate in the literature.[11,27] The discrepancy is not large and does not markedly affect use of the constant in the Marcus relationship, where it appears as a square-root term. However, the apparent self-exchange rate determined from the rate of racemization of $[Co(phen)_3]^{3+}$ catalyzed by $[Co(phen)_3]^{2+}$, $k_{\Delta\Lambda}$, may differ from k_{11} by a factor determined by the extent of stereoselectivity in the reaction. An attempt was made to obtain an independent measure of k_{11} by NMR line broadening. The ^1H NMR spectrum of $[Co(phen)_3]^{3+}$ displays a sharp singlet at 8.5 ppm (due to the H_5 and H_6 protons on the phenanthroline). The width of this peak is not perceptibly altered in the presence of 5.6×10^{-3} M $[Co(phen)_3]^{2+}$, the limit of solubility of the paramagnetic reductant in 0.1 M nitrate solutions containing $[Co(phen)_3]^{3+}$. While this does not provide a measure of the self-exchange rate, it indicates an upper limit for k_{11} of 100 M^{-1} s^{-1}, in line with the value from circular dichroism studies.

Measurement of the rate of exchange using radioactive ^{60}Co and the separation method based on the extraction of the cobalt(II) thiocyanate complex[3] gives rates slower than those reported earlier.[3] To achieve measurable rates by radioactive exchange requires that the concentrations of the complexes be of the order of 10^{-5}–10^{-4} M, and the system is much more prone to error at these concentrations than at the higher concentrations used in the optical rotation experiments. The dependence of the rate of exchange was not cleanly first-order in either reactant but approached first-order as the concentrations increased. On this basis, a limiting value of $k_{11} \leq 3.4$ M^{-1} s^{-1} at 25 °C in 0.01 M KNO_3 can be set.[28] Within the error of both types of experiments, this number agrees with the value for $k_{\Delta\Lambda}$ in Table III. It is concluded that stereoselectivity, if present in this reaction, is relatively unimportant.

Self-exchange rates for $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$ and $[Co(5,6\text{-}Me_2phen)_3]^{3+/2+}$ were determined over a range of concentrations narrower than those for $[Co(phen)_3]^{3+/2+}$. There is a first-order dependence on [cobalt(II)], and the second-order rate constants are 120 ± 20 M^{-1} s^{-1} and 300 ± 50 M^{-1} s^{-1}, respectively, at 25.0 °C in 0.10 M nitrate media. Previous estimates[10–12] of the self-exchange rates for these two systems vary from 0.77 to 600 M^{-1} s^{-1} for $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$ and from 0.05 to 40 M^{-1} s^{-1} for $[Co(5,6\text{-}Me_2phen)_3]^{3+/2+}$ and are thus difficult to compare with the present work. However, it is noteworthy that the self-exchange rates are 1 order of magnitude higher than those for the parent $[Co(phen)_3]^{3+/2+}$ system, explaining difficulties encountered[21] in the detection of stereoselectivity by using these methyl-substituted reagents. It is also noteworthy that the trend in the self-exchange rates $[Co(5,6\text{-}Me_2phen)_3]^{3+/2+} > [Co(4,7\text{-}Me_2phen)_3]^{3+/2+} > [Co(phen)_3]^{3+/2+}$ reflects the order of increasing solubility of the complexes and suggests that solvent reorganization in the reactions may be a dominant feature.

(c) Stereoselectivity Experiments. The nature of the self-exchange reactions precludes direct determination of any stereoselectivity associated with them. However, differences in the circular dichroism spectra of the three cobalt(III) phenanthroline derivatives are sufficiently large to allow the detection of chiral induction in the oxidation of the complexes $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ and $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ by $[Co(phen)_3]^{3+}$. Detection of stereoselectivity will depend on whether the rate of the cross-reaction is significantly greater than the self-exchange rate of the expected optically active product. Determination of the cross-reaction rates by conventional stopped-flow spectrophotometry presents some difficulties, because the complexes exhibit very similar visible absorption changes and the ultraviolet region is complicated by the large excess of free ligand necessary to ensure quantitative complex formation of the labile reductant. The reactions were examined by making use of the decay in the circular dichroism spectrum of the optically active $[\Lambda\text{-}(+)_{589}\text{-}Co(phen)_3]^{3+}$ under pseudo-first-order conditions, with an excess of $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ or $[Co(5,6\text{-}Me_2phen)_3]^{2+}$. In the case of [Co-

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(23) In investigations of the effects of specific anions on reaction rates, constant anion concentration provides a medium that is sensibly constant and is preferred over the more usual constant ionic strength.

(24) An empirical description of the second-order rate constants yields the expression $k_{\Delta\Lambda} = 1.5 + 32[Cl^-]$ in chloride media and $k_{\Delta\Lambda} = 1.5 + 156[NO_3^-]/(1 + 6.7[NO_3^-])$ in nitrate media, but the significance of the parameters is unclear.

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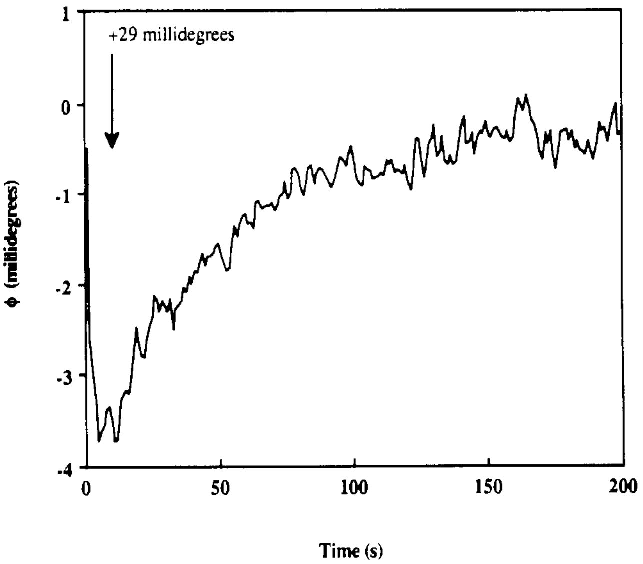

Figure 4. Decay of the circular dichroism signal (ϕ, mdeg) at 480 nm after the reaction of $[\Lambda\text{-}(+)_{589}\text{-}Co(phen)_3]^{3+}$ (6.2×10^{-5} M) with [*rac*-$Co(4,7\text{-}Me_2phen)_3]^{2+}$ (1.7×10^{-4} M) in 0.10 M nitrate media at 25.0 °C.

$(5,6\text{-}Me_2phen)_3]^{2+}$, the rate shows the expected dependence on [cobalt(II)] with a second-order rate constant of 430 ± 20 M^{-1} s^{-1} at 25.0 °C in 0.10 M nitrate media. The reaction with $[Co(4,7\text{-}Me_2phen)_3]^{3+}$ is somewhat faster and is at the limit of the data acquisition system for the instrument; however, a second-order rate constant of $(2 \pm 1) \times 10^3$ M^{-1} s^{-1} is estimated from the half-life.

The rate of the cross-reaction of $[Co(phen)_3]^{3+}$ with $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ is comparable with the self-exchange rate of $[Co(5,6\text{-}Me_2phen)_3]^{3+/2+}$. However, with $[Co(4,7\text{-}Me_2phen)_3]^{2+}$, the cross-reaction rate is 1 order of magnitude faster than the self-exchange rate of $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$ and should allow detection of stereoselectivity. The circular dichroism response at 480 nm during the time course of the reaction of $[\Lambda\text{-}(+)_{589}\text{-}Co(phen)_3]^{3+}$ wih $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ is presented in Figure 4. The signal starts at +29 mdeg and rapidly decreases to −4 mdeg as $[\Lambda\text{-}(+)_{589}\text{-}Co(phen)_3]^{3+}$ oxidizes $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ (eq 8).

$$[\Lambda\text{-}Co(phen)_3]^{3+} + [Co(4,7\text{-}Me_2phen)_3]^{2+} \rightarrow [Co(phen)_3]^{2+} + [Co(4,7\text{-}Me_2phen)_3]^{3+} \quad (8)$$

This latter signal subsequently decays to the base line at the rate of the self-exchange reaction of $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$. In other words, the $[Co(4,7\text{-}Me_2phen)_3]^{3+}$ formed in the reaction of $[\Lambda\text{-}(+)_{589}\text{-}Co(phen)_3]^{3+}$ with $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ is around 15% optically active and has the configuration opposite from that of $[\Lambda\text{-}(+)_{589}\text{-}Co(phen)_3]^{3+}$, a 15% ΔΛ process.

Chiral induction in these reactions between two cationic metal–phenanthroline derivatives is significant and suggests that there must be intimate contact between the reagents during the electron-transfer process, despite the fact that both complexes are cationic.[29] Interestingly, the nature of the chiral induction is the same, ΔΛ, as that noted[30] in ion-triplet interactions between $[Ru(phen)_3]^{2+}$ complexes in sulfate media, where a model for the interaction was proposed from NMR measurements. The location of anions in these triplets may be inferred from crystal structure information.[31,32]

Table IV. Observed and Calculated Second-Order Rate Constants for Self-Exchange Reactions and Cross-Reactions of $[Co(terpy)_2]^{3+/2+}$ and $[Co(phen)_3]^{3+/2+}$ and Its Substituted Derivatives at 25.0 °C and 0.10 M Ionic Strength ($NaNO_3$)

		k, M^{-1} s^{-1}	
oxidant	reductant	obsd	calcd[a]
$[Co(phen)_3]^{3+}$	$[Co(phen)_3]^{2+}$	12.0 ± 0.3	
$[Co(phen)_3]^{3+}$	$[Co(4,7\text{-}Me_2phen)_3]^{2+}$	2000 ± 1000	1430
$[Co(phen)_3]^{3+}$	$[Co(5,6\text{-}Me_2phen)_3]^{2+}$	430 ± 20	640
$[Co(4,7\text{-}Me_2phen)_3]^{3+}$	$[Co(4,7\text{-}Me_2phen)_3]^{2+}$	120 ± 20	
$[Co(5,6\text{-}Me_2phen)_3]^{3+}$	$[Co(5,6\text{-}Me_2phen)_3]^{2+}$	3000 ± 50	
$[Co(phen)_3]^{3+}$	$[Co(terpy)_2]^{2+}$	83 ± 6[b]	
$[Co(terpy)_2]^{3+}$	$[Co(4,7\text{-}Me_2phen)_3]^{2+}$	867 ± 16[c]	
$[Co(terpy)_2]^{3+}$	$[Co(5,6\text{-}Me_2phen)_3]^{2+}$	478 ± 8[c]	
$[Co(terpy)_2]^{3+}$	$[Co(terpy)_2]^{2+}$		50

[a] The following radii were used: $[Co(phen)_3]^{3+}$, 7 Å; $[Co(4,7\text{-}Me_2phen)_3]^{2+}$, 8 Å; $[Co(5,6\text{-}Me_2phen)_3]^{2+}$, 8 Å; $[Co(terpy)_2]^{3+}$, 7 Å. [b] A value of 416 M^{-1} s^{-1} in 0.5 M chloride media is reported for this reaction in ref 14. [c] Reference 21.

Although stereoselectivity was not detected in the self-exchange reactions, it seems likely that effects comparable in magnitude to those in the cross-reactions might be expected. If the stereoselectivities for the self-exchange reactions are in the region of 15% ΔΛ, then it should be borne in mind that the rates evaluated from the cobalt(II)-catalyzed racemization of the cobalt(III) complexes are 15% higher[33] than those evaluated by other methods.

(d) Marcus Treatment. Observed and calculated second-order rate constants for the self-exchange reactions and cross-reactions studied are collected in Table IV. Outer-sphere electron-transfer reactions of these metal–phenanthroline complexes are readily described by the Marcus expression,[34] which is generally used in the form of eqs 9 and 10, where ΔG^{**} is the electrostatically

$$\Delta G_{12}^{**} = \tfrac{1}{2}[\Delta G_{11}^{**} + \Delta G_{22}^{**} + \Delta G^\circ(1 + \alpha^{**})] \quad (9)$$

$$\alpha^{**} = \Delta G^\circ / 4(\Delta G_{11}^{**} + \Delta G_{22}^{**}) \quad (10)$$

corrected free energy of activation and ΔG° is the electrostatically corrected free energy change for the reaction. The self-exchange rates evaluated in this study yield rates for the oxidation of $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ and $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ by $[Co(phen)_3]^{3+}$ of 1430 and 640 M^{-1} s^{-1}, respectively, in good agreement with the experimental observations. Reactions of $[Co(terpy)_2]^{2+}$ with $[Co(phen)_3]^{3+}$ and $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ and $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ with $[Co(terpy)_2]^{3+}$ have also been studied,[21] and the rates are consistent with a self-exchange rate for $[Co(terpy)_2]^{3+/2+}$ of 50 M^{-1} s^{-1}, in fair agreement with the accepted value of 400 M^{-1} s^{-1}.[3,4,11]

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Supplementary Material Available: Lists of pseudo-first-order rate constants for the self-exchange reactions of $[Co(phen)_3]^{3+/2+}$ and its derivatives and the cross-reactions of $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ and $[Co(terpy)_2]^{2+}$ with $[Co(phen)_3]^{3+}$ (Tables SI and SII) (6 pages). Ordering information is given on any current masthead page.

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