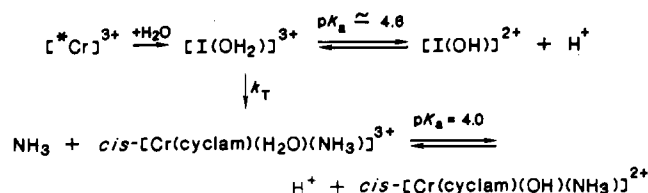
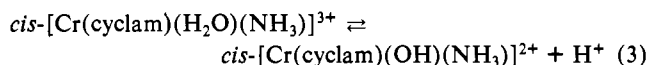


Scheme I



coordinated to a chromium(III) center<sup>10</sup> and thus indicative of the reaction



Below pH 3, the equilibrium will lie to the left side so that now the net decrease in conductivity will *only* reflect the reaction of proton with released ammonia (eq 2). By comparison of the signal levels here with those arising from the photorelease of ammonia from  $[Cr(NH_3)_6]^{3+}$  ( $\phi = 0.45$ ),<sup>11</sup> the quantum yields for ammonia formation on irradiation of the first and second quartet bands are found to be  $0.16 \pm 0.04$  (3) and  $0.14 \pm 0.02$  (3), respectively, in agreement with the value 0.2, measured under steady-state photolytic conditions.<sup>7</sup> These features substantiate that the formations of  $cis-[Cr(cyclam)(H_2O)(NH_3)]^{3+}$  and free ammonia are being observed here.

Because none of the conductivity changes occur with rates exceeding that for decay of the doublet state, one can conclude that the nascently populated quartet states are chemically unreactive; i.e., greater than 90% of the formation of ammonia arises in association with the decay of the emitting doublet level. This state's central role is further shown by results obtained in quenching experiments with  $K_3[Cr(CN)_6]$ : this compound does not absorb significantly at the excitation wavelength of 530 nm, and its lowest doublet level, which is chemically unreactive, lies below that for the cyclam complex.<sup>12</sup> The quenching of the latter's emission under steady-state irradiation is well described by a Stern-Volmer plot having a slope of  $(9.2 \pm 0.3) \times 10^3 M^{-1}$ . Under conditions where 48% of the emission is quenched, a corresponding decrease in the net conductivity level of  $49 \pm 4\%$  occurs at pH 2.8. The quenching is a dynamical process as shown by the fact that the associated rate constants are the same for emission and conductivity:  $(7.0 \pm 0.8) \times 10^9$  and  $(6.4 \pm 0.9) \times 10^9 M^{-1} s^{-1}$ , respectively.

A key observation in regard to the reaction mechanism is that the rate of emission decay always exceeds that for the formation of the aquochromium product: the closest approach in these rates occurs in the plateau region of Figure 2, where  $k(em)/k(cond) = (2.7 \pm 0.4)/1$ . This feature is *not* consistent with mechanisms commonly proposed to explain the photobehavior of related chromium(III) amine systems, namely, ones involving formation of the final product directly from the decay of the doublet state or from a rate-limiting bisc process to a low-lying quartet level, followed by prompt chemical reaction, because both situations require at pHs below 4, where the rate of ammonia protonation is not rate-limiting, that  $k(cond)$  should be equal to  $k(em)$ . The fact that  $k(em)$  is always greater than  $k(cond)$  indicates that there is formation of an intermediate from the decay of the doublet state and that this intermediate subsequently reacts to give the final chromium(III) aquo product of eq 1.

We propose the mechanism given by Scheme I, where the chemistry begins with the decay of the doublet state  $[^*Cr]^{3+}$ : for clarity, the reaction steps regenerating the starting material from the decay of  $[^*Cr]^{3+}$  and perhaps also from that of the intermediate are not shown.

The intermediate  $[I(OH_2)]^{3+}$  is proposed to involve the coordination of a water molecule and to exhibit its own rapidly es-

tablished acid-base reaction in order to account for the following features. A nascent increase in conductivity occurs over the pH range of 5.4 to ca. 4, and this represents an increase in proton concentration. The rate of this increase is the same as that for the decay of emission; however, the maximum level in conductivity drops on progressing from pH 5.4 to ca. 4, as shown in the insert of Figure 2 (open squares). The shape of this plot suggests that  $[I(OH_2)]^{3+}$  exhibits a  $pK_a$  around 4.6. Ammonia release is portrayed as being in association with the formation of the final chromium(III) aquo product rather than with that of  $[I(OH_2)]^{3+}$  because, if the latter situation prevailed, then at pHs  $\leq 3$  the rate of the conductivity decrease through protonation of ammonia (eq 2) would now be the same as that for the emission decay: this is not in accord with the experimental findings.

The value of the rate constant  $k_T$  for the conversion of  $[I(OH_2)]^{3+}$  into  $cis-[Cr(cyclam)(H_2O)(NH_3)]^{3+}$  will be closely approximated by the limiting value of  $k(cond)$  (Figure 2), and this implies that, at pHs below 3, the effective lifetime of  $[I(OH_2)]^{3+}$  is about  $3 \mu s$ .<sup>13</sup> Is this intermediate an excited-quartet-state species formed by a bisc process or is it a ground-state entity? In regard to the first alternative, no emission (aside from that for the doublet state) has been found up to 800 nm whereas such might be expected for a long-lived excited quartet state. Indeed, quartet states are generally perceived to be very short lived, in contrast to the intermediate's considerable longevity.<sup>1-5,14</sup> Given the facile quenching by  $[Cr(CN)_6]^{3-}$  of the doublet state, which is shorter lived than the intermediate, then the expectation from spin correlation is that  $[Cr(CN)_6]^{3-}$  should also be an effective quenching agent toward the chemical reactive intermediate if it were in an electronically excited quartet state. The consequence would be that the percentage of emission quenching should be less than that for the quenching of the chemical reaction, but this is not found here. These features militate against an excited-state description of the intermediate and perforce favor its designation as being a ground-state species.

**Acknowledgment.** We wish to express our appreciation to the Natural Sciences and Engineering Council of Canada for financial support, to Dr. F. Wasgestian for providing the  $K_3[Cr(CN)_6]$  sample used in this study, and to Dr. N. A. P. Kane-Maguire for his comments and assistance.

**Registry No.**  $cis-[Cr(cyclam)(NH_3)_2]^{3+}$ , 94536-68-2;  $cis-[Cr(cyclam)(H_2O)(NH_3)]^{3+}$ , 94536-66-0;  $NH_3$ , 7664-41-7.

- (13) Because  $cis-[Cr(cyclam)(NH_3)_2]^{3+}$  undergoes rapid thermal aquation in basic solutions, it was not experimentally possible to determine if  $[I(OH_2)]^{3+}$  undergoes direct conversion to  $cis-[Cr(cyclam)(OH)(NH_3)]^{2+}$ .
- (14) Rojas, G. E.; Dupuy, C.; Sexton, D. A.; Magde, D. *J. Phys. Chem.* **1986**, *90*, 87-92.
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Received November 4, 1987

### Electron-Transfer Rates of a Co(-I)/Co(0) Couple and Crystal Structure of the Tetrakis(trimethyl phosphite)cobaltate(-I) Ion

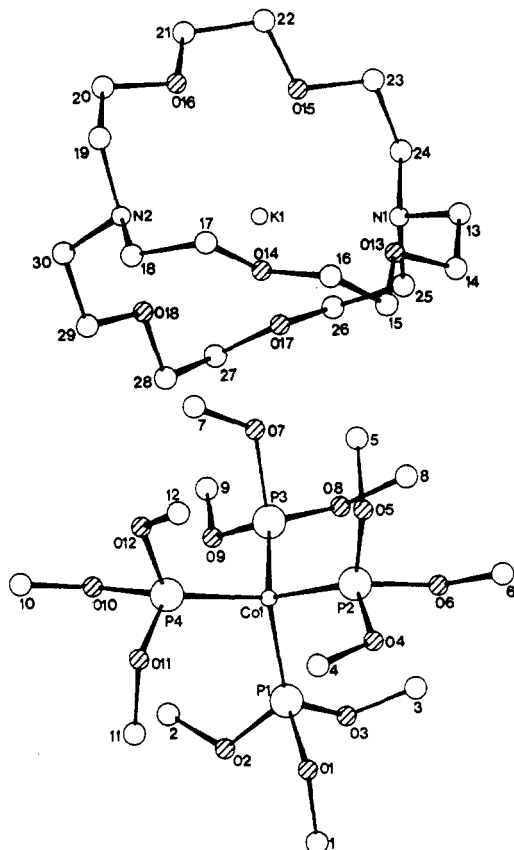
Sir:

The determination of self-exchange rates has been an important facet of the study of electron-transfer reactions in inorganic chemistry.<sup>1</sup> However, much of the available data is restricted

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**Figure 1.** Molecular structure of  $[\text{K}(222)]^+[\text{Co}[\text{P}(\text{OMe})_3]_4]^-$  showing the spatial relationship of the ions in the crystal. The average Co-P bond distance is 2.06 Å, and the average P-Co-P angle is 109.5°.

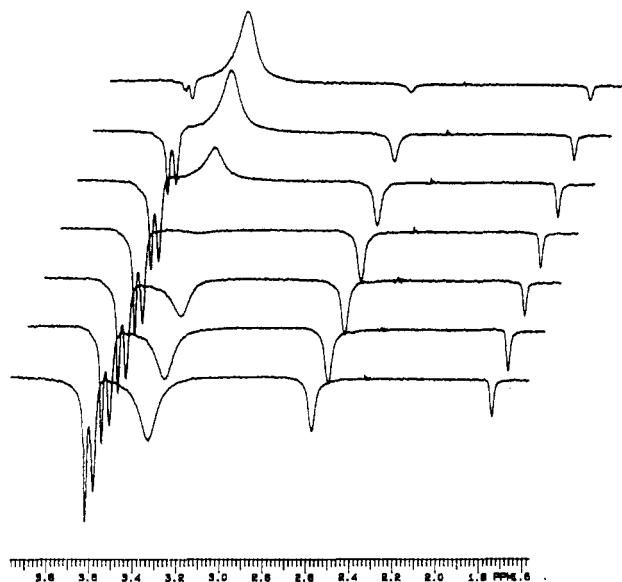
to coordination compounds featuring octahedral coordination of the metal with hard (nitrogen- or oxygen-based) ligands. A wealth of measurements exists, for example, concerning  $\text{CoL}_6^{3+/2+}$  couples (where L is a nitrogen base), but little is known about the facility of electron transfer between cobalt complexes in other coordination environments and less common oxidation states. We have recently measured self-exchange rates for tetrahedral cobalt alkyls in unusually high oxidation states (III, IV, and V).<sup>2</sup> Herein we report the characterization of an extremely low-valent redox couple based on cobalt in a tetrahedral environment of phosphorus donors.

Following an earlier report by Muettterties and Hirsekorn,<sup>3</sup> deprotonation of the cobalt hydride  $\text{HCo}[\text{P}(\text{OMe})_3]_4$  with KH yielded an insoluble material of the composition  $\text{KCo}[\text{P}(\text{OMe})_3]_4$ . We have found that treatment of this solid with 1 equiv of cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) results in a complex that is readily soluble in THF.  $[\text{K}(222)]^+[\text{Co}[\text{P}(\text{OMe})_3]_4]^-$  was isolated as air-sensitive colorless crystals in essentially quantitative yield and has been characterized by standard analytical and spectroscopic techniques as well as by determination of its crystal structure (see Figure 1).<sup>4</sup>

The crystal consists of well-separated cations and anions. The potassium cation resides symmetrically within the cryptand cavity (average K-O and K-N distances are 2.83 and 2.96 Å, respectively).<sup>5</sup> The cobalt complex ion exhibits the tetrahedral structure

**Table I.** Electron-Transfer Rate Constants Determined by Line-Shape Analysis of  $^1\text{H}$  NMR Spectra

$T$ , K	$k_{\text{et}}$ , $\text{M}^{-1} \text{s}^{-1}$	$T$ , K	$k_{\text{et}}$ , $\text{M}^{-1} \text{s}^{-1}$
335.5	42300	294.3	8800
325.5	28900	284.2	5280
315.4	21100	274.1	3170
305.3	13900	264.9	1620



**Figure 2.** Stacked plot of seven  $^1\text{H}$  NMR spectra comprising one "nonselective inversion recovery experiment" for the determination of  $T_{1,\text{obsd}}$  (here at 254 K). The asterisk marks the phosphite methyl proton resonance of the diamagnetic  $[\text{K}(222)]^+[\text{Co}[\text{P}(\text{OMe})_3]_4]^-$ .

expected of a four-coordinate  $d^{10}$  system. The cobalt-phosphorus bond distances (ca. 2.06 Å) are very short compared to other reported values (see below), indicating significant strengthening of the Co-P bond by  $d\pi-d\pi$  back-donation.

The cyclic voltammogram of  $[\text{K}(222)]^+[\text{Co}[\text{P}(\text{OMe})_3]_4]^-$  in THF showed a reversible oxidation wave at  $-1.77$  V versus  $\text{Fc}^+/\text{Fc}$ . The product of a one-electron oxidation,  $\text{Co}[\text{P}(\text{OMe})_3]_4$ , had indeed been prepared earlier in low yield by reduction of  $\text{CoCl}_2$  in the presence of  $\text{P}(\text{OMe})_3$ .<sup>6</sup> We have found that this 17-electron complex may be prepared much more conveniently by oxidation of  $\text{KCo}[\text{P}(\text{OMe})_3]_4$  with 0.5 equiv of  $\text{Pb}(\text{OAc})_2$  at low temperature ( $-78$  °C to ambient). The molar magnetic susceptibility  $\chi_m$  of solid  $\text{Co}[\text{P}(\text{OMe})_3]_4$  was measured in the temperature interval 3–300 K.<sup>7</sup> The room-temperature magnetic moment  $\mu_{\text{eff}}$  of 2.20  $\mu_B$  was consistent with the presence of one unpaired electron. In accord with the earlier report,<sup>6</sup> solutions of  $\text{Co}[\text{P}(\text{OMe})_3]_4$  exhibited a single broad resonance in the  $^1\text{H}$  NMR spectrum at approximately 0 ppm. The chemical shift of this resonance varied linearly with  $1/T$ , consistent with the radical nature of  $\text{Co}[\text{P}(\text{OMe})_3]_4$ .

The  $^1\text{H}$  NMR spectrum of an equimolar THF- $d_8$  solution of  $[\text{K}(222)]^+[\text{Co}[\text{P}(\text{OMe})_3]_4]^-$  and  $\text{Co}[\text{P}(\text{OMe})_3]_4$  (both 0.071 M) at 60 °C exhibited only one broad resonance attributable to phosphite methyl groups. At this temperature the degenerate electron transfer, which interconverts the two complexes, is fast on the NMR time scale. Lowering of the temperature resulted first in a broadening and subsequently in a splitting of this resonance into the two resonances characteristic of  $[\text{K}(222)]^+[\text{Co}[\text{P}(\text{OMe})_3]_4]^-$  and  $\text{Co}[\text{P}(\text{OMe})_3]_4$ , respectively. Coalescence of the two peaks was observed at 32 °C. The experimental spectra in the temperature range +60 to  $-10$  °C were fit with line shapes

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 (4)  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  3.61 (s, 12 H), 3.57 (t, 12 H), 3.34 (m, 36 H), 2.58 (t, 12 H);  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta$  71.2, 68.4, 54.7, 49.1 (OCH<sub>3</sub>). Anal. Calcd for  $\text{C}_{30}\text{H}_{72}\text{CoKN}_2\text{O}_{18}\text{P}_4$ : C, 37.11; H, 7.49; N, 2.89; P, 12.76. Found: C, 36.89; H, 7.69; N, 2.89; P, 11.54. Crystal data: colorless crystals from THF; orthorhombic *Pbca*;  $a = 20.924$  (17) Å,  $b = 21.022$  (3) Å,  $c = 21.483$  (6) Å;  $\alpha = \beta = \gamma = 90^\circ$ ;  $Z = 8$ ;  $R = 0.038$ ,  $R_w = 0.040$ . Details of the structure determination will be described in a full paper.

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(7) The susceptibility data was fitted with a Curie-Weiss expression ( $\chi_m = C/[T - \theta]$ ).  $C = 0.604$  emu K/mol,  $\theta = 0.6$  K.

**Table II.** Electron-Transfer Rate Constants Determined by a "Nonselective Inversion Recovery Experiment"

$T, K$	$T_{1,dia}, s$	$T_{1,para}, s$	$T_{1,obsd}, s$	$k_{et}, M^{-1} s^{-1}$
273.0	1.32	1.10	0.0063	2439
264.0	1.12	1.11	0.0078	1957
254.0	0.95	1.063	0.0114	1327
243.3	0.86	0.904	0.0197	751
233.3	0.78	0.737	0.0369	379
223.3	0.78	0.570	0.0563	228
213.7	0.88	0.410	0.0804	137
203.7	1.01	0.321	0.105	84
194.2	1.20	0.262	0.145	35

<sup>a</sup>Concentration of both reactants was 0.065 M (spectrometer frequency 400 MHz).

generated by the computer program DNMR-5.<sup>8</sup> The second-order rate constants for the self-exchange reaction thus obtained are listed in Table I.

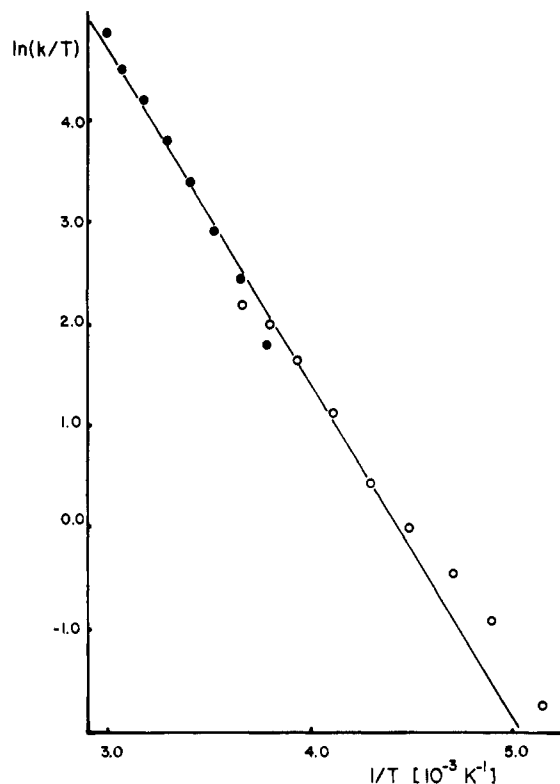
Attempts to extend the range of measured rate constants into the limiting slow exchange regime by using 2D NOESY exchange spectroscopy<sup>9</sup> were foiled by the extremely fast relaxation of the protons in paramagnetic  $Co[P(OMe)_3]_4$  ( $T_1 < 1$  ms). However, this obstacle could be turned into an advantage in a "nonselective inversion recovery experiment".<sup>10</sup> Irradiation of the mixture with an indiscriminate  $180^\circ$  pulse followed by collection of spectra after various specific delay times allowed the determination of the longitudinal relaxation time  $T_{1,obsd}$  of the phosphite protons in diamagnetic  $[K(222)]^+[Co[P(OMe)_3]_4]^-$ . A series of spectra comprising one such experiment is depicted in Figure 2. The three processes contributing to the relaxation are dipole-dipole coupling (characterized by the longitudinal relaxation time for  $[K(222)]^+[Co[P(OMe)_3]_4]^-$  measured in the absence of  $Co[P(OMe)_3]_4$ , here  $T_{1,dia}$ ), interaction with the paramagnetic  $Co[P(OMe)_3]_4$  ( $T_{1,para}$ , which is the inverse of a pseudo-first-order rate constant and hence depends on the concentration of  $Co[P(OMe)_3]_4$ ), and electron transfer ( $T_{1,et}$ ; concentration dependent in the same fashion). This experiment was simplified greatly by the fast relaxation of the paramagnetic reactant, because longitudinal magnetization of the nuclear spins in it decayed too fast to transfer to the diamagnetic site. We could thus directly measure the rate of the forward electron transfer from  $[K(222)]^+[Co[P(OMe)_3]_4]^-$  to  $Co[P(OMe)_3]_4$  without any interference from the reverse process.

In order to extract self-exchange rate constants from the relaxation times, all other contributions to the relaxation had to be subtracted according to eq 1. Table II lists the results of mea-

$$1/T_{1,et} = 1/T_{1,obsd} - 1/T_{1,dia} - 1/T_{1,para} \quad (1)$$

surements of the longitudinal relaxation times of  $[K(222)]^+[Co[P(OMe)_3]_4]^-$  in the absence of a paramagnetic compound (i.e.  $T_{1,dia}$ ). We have also determined  $T_1$  in the presence of the paramagnetic complex  $Co(PMe)_3$ .<sup>11</sup> This complex was chosen because it is a very close analogue of  $Co[P(OMe)_3]_4$  in a structural and magnetic sense but is not reduced by  $[K(222)]^+[Co[P(OMe)_3]_4]^-$ .<sup>12</sup> Factoring  $T_{1,dia}$  and the concentration difference out of the latter data yielded the required values of  $T_{1,para}$  (also listed in Table II). Finally, evaluation of eq 1 and division of the so obtained pseudo-first-order rate constant by the concentration of  $Co[P(OMe)_3]_4$  gave the second-order rate constants for the degenerate electron transfer ( $k_{et}$ ).

Figure 3 shows the Arrhenius plot of the rate constants over a 140 K temperature range. The enthalpy of activation is small



**Figure 3.** Arrhenius plot of rate constants for the degenerate self-exchange reaction. Filled circles represent data from line-shape analysis and open circles derive from inversion recovery experiments. The lowest three points were not included in the calculation of the regression line, because their uncertainty is the largest (electron-transfer contribution to relaxation becomes small).

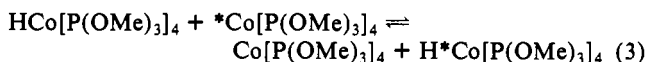
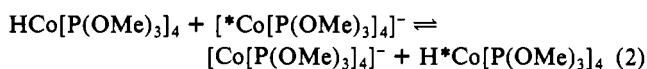
( $\Delta H^\ddagger = 6.6$  (2) kcal/mol) and the negative entropy of activation ( $\Delta S^\ddagger = -18.3$  (7) eu) is typical of electron-transfer reactions between metal complexes. A comparison of the experimental activation parameters with a barrier height predicted by Marcus theory<sup>13</sup> required information about the extent of structural change upon electron transfer. Whereas the Co-P distance in  $[K(222)]^+[Co[P(OMe)_3]_4]^-$  was known (see above), the corresponding value for  $Co[P(OMe)_3]_4$  could not be determined due to a disorder problem.<sup>6</sup> Such distances range from 2.16 to 2.23 Å in structurally characterized phosphine or phosphite complexes of zerovalent cobalt.<sup>14</sup> The closest analogue to  $Co[P(OMe)_3]_4$  was  $Co(MA)[P(OMe)_3]_3$  (MA = maleic anhydride) with a Co-P distance of 2.17 Å.<sup>14a</sup> We used this value in a Marcus type calculation<sup>15</sup> and obtained a predicted activation barrier of  $\Delta G^\ddagger = 8.6$  kcal/mol. At 25 °C the experimental value was  $\Delta G^\ddagger = 12.0$  kcal/mol. Given the uncertainty in the estimates incorporated in the calculation, we consider this reasonable agreement.

We have measured rates of degenerate electron transfer for a nontraditional redox couple over a large temperature interval. Marcus theory seems to provide a satisfactory framework for the prediction of these rates. We are currently investigating degen-

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 (15) See ref 13b for details of the calculation. The following parameters were used:  $d(Co^{I}-P) = 2.06$  Å,  $d(Co^0-P) = 2.17$  Å; force constants [using Badger's rule (Badger, R. M. *J. Chem. Phys.* 1934, 2, 128; 1935, 3, 710), calibrated with data for  $Ni(PF_3)_4$  (Bligh-Smith, R. M.; Edwards, H. G. M.; Fawcett, V. *Spectrochim. Acta, Part A* 1987, 43A, 1069)],  $k(Co^{I}-P) = 4.4 \times 10^{-5}$  dyn/cm,  $k(Co^0-P) = 2.8 \times 10^{-5}$  dyn/cm, complex radius 6.0 Å.  $\Delta G_c^\ddagger = 0$  kcal/mol;  $\Delta G_i^\ddagger = 6.0$  kcal/mol;  $\Delta G_o^\ddagger = 2.6$  kcal/mol.

erate transfers of other small particles in this system, e.g. protons (eq 2) and hydrogen atoms (eq 3). It will be interesting to see what parallels, if any, exist between these formally analogous reactions.



**Acknowledgment.** This research was supported by grants from the National Science Foundation (CHE-8451670 and CHE-8512710), Dow Chemical Co., and Cornell University.

**Registry No.** [K(222)]<sup>+</sup>[Co[P(OMe)<sub>3</sub>]<sub>4</sub>]<sup>-</sup>, 113219-24-2; K[Co[P(OMe)<sub>3</sub>]<sub>4</sub>], 51371-41-6; Co[P(OMe)<sub>3</sub>]<sub>4</sub>, 15906-77-1; Pb(OAc)<sub>2</sub>, 301-04-2.

**Supplementary Material Available:** Summary of the X-ray analysis and tables of fractional coordinates and isotropic temperature factors, bond distances, bond angles, torsion angles, and anisotropic temperature factors for [K(222)]<sup>+</sup>[Co[P(OMe)<sub>3</sub>]<sub>4</sub>]<sup>-</sup> (10 pages); a table of structure factors (32 pages). Ordering information is given on any current masthead page.

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## Articles

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### Quantitative Aspects of Pfeiffer Effect Optical Activity in Aqueous Dysprosium(III) Complexes with 2,6-Pyridinedicarboxylic Acid

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Received October 2, 1987

Under the assumptions that the addition of a chiral "environment compound" simply shifts the racemic equilibrium of labile enantiomers and does not preferentially quench enantiomeric excited states, it is demonstrated that the measurement of the circularly polarized luminescence (CPL) from racemic solutions using circularly polarized excitation, combined with the circular dichroism (CD) and CPL of the solution after the addition of the chiral adduct, can yield quantitative information concerning the equilibrium shift and the optical activity of the individual enantiomers. This is demonstrated for the equilibrium between  $\Delta$  and  $\Lambda$  isomers of Dy(2,6-pyridinedicarboxylate = DPA)<sub>3</sub><sup>3-</sup> where the added chiral species is L-histidine. For this system we report the resultant enantiomeric excess and the dissymmetry ratios for selected electronic transitions of pure enantiomers, even though they cannot be resolved chemically.

#### Introduction

The "Pfeiffer effect" has as its origin the work of Pfeiffer and others on the enhancement in optical activity in solutions composed of a chiral "environment compound" and a racemic but kinetically labile metal complex.<sup>1-3</sup> This original work involved primarily transition-metal tris complexes with the bidentate ligands 2,2'-bipyridine and 1,10-phenanthroline, and the chiral environment compound was usually an alkaloid. In these early studies, and in most reports until very recently, the enhancement of optical activity was monitored through the measurement of optical rotation. It was later realized that the observed phenomenon was caused by a shift in the racemic equilibrium constant of the metal complex caused by the chiral environment compound, as evidenced by the appearance of circular dichroism (CD) in the spectral region corresponding to d-d absorptions.<sup>4</sup> The CD spectra obtained were in some cases identical with those of previously resolved enantiomers.<sup>5</sup>

In recent years, Brittain has demonstrated that, in racemic lanthanide tris complexes with 2,6-pyridinedicarboxylate (DPA), optical activity can be enhanced as measured by the circular polarization in the luminescence (CPL) from f-f emissive transitions.<sup>6-11</sup> This effect has been observed for a wide variety of

added chiral agents. Because these lanthanide complexes are generally more labile than the transition-metal complexes used in the original demonstration of Pfeiffer effect optical activity and because the coordination numbers of the lanthanide complexes are so variable, it is not clear that all of the reports of induced optical activity in these lanthanide complexes can be classified as simply a racemic equilibrium disturbance. In addition, because CPL is inherently an *excited-state* effect, one cannot rule out the possibility that the added chiral species is disturbing the emitting-state population instead of that of the ground state. At the present time, there exists no uniformly accepted classification as to what exactly constitutes a "Pfeiffer effect" for lanthanides.<sup>12</sup>

Recently, we have reported CPL spectra from racemic Ln-(DPA)<sub>3</sub><sup>3-</sup> solutions in which an optically active excited-state population was generated by employing a circularly polarized excitation beam.<sup>13,14</sup> This experiment is possible only if the emitting-state population is inert to racemization during the lifetime of the excited species. The fact that we observe CPL from the racemate without any added species allows us the opportunity to compare CPL spectra before and after the addition of chiral environment compounds. In those cases where the spectra are very similar, one can conclude that a simple equilibrium shift has

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