steady-state concentration of CO is unusual for reactions resulting from metal–carbonyl bond dissociation (e.g. ligand substitution) because there is usually a stoichiometric increase in [CO] in such reactions.) As a result of the low concentration of CO in the solution of reaction 4, coordination of the very poor ligand, $CpW(CO)_3Me$ (eq 6) is competitive with the back-reaction of $CpW(CO)_2Me$ with CO (eq 5).

Table II shows a comparison of the observed values of ϕ compared with those calculated from eq 3. The value of ϕ_p was assumed to be 0.40, the quantum yield for ligand substitution. The rate constants k_{-1} and k_2 were set so as to let ϕ_{calcd} equal ϕ_{obsd} for the case in which wavelength is equal to 405 nm. It can be seen that the quantum yield is in fact lowered by increasing the extinction coefficient and intensity, although not to as great an extent as predicted. Several factors could substantially detract from the agreement between predicted and observed values in the use of eq 3: (1) the inability to reproducibly focus the lamp on the reaction cell will result in an effective variability of A; (2) stirring may occur on a time scale competitive with the lifetimes of the intermediates (this will decrease the effect of A and ϵ on the observed values); (3) in the particular case of reactions 5 and 6, a buildup of CO in solution, perhaps due to a side reaction, would result in an overall rate of back-reaction less dependent on intensity, A, and ϵ.

Conclusion. Certain photochemical pathways involve a competition between elementary reactions that are first and second order in a short-lived intermediate. The observed quantum yields of such reactions may show a dependency on irradiation parameters such as optical density, extinction coefficient, irradiation intensity, and window area. Difficulties may be encountered in attempting to quantitatively apply the above equations with any precision. Nevertheless, we believe that they can be quite useful, if only for calculating the expected direction and order of magnitude of any dependency of the quantum yield on these irradiation parameters. At the very least, the photochemical experimenter should always be aware of the possibility that the parameters discussed herein can affect efficiencies and even product distributions.

Experimental Section

Quantum yield measurements for the binuclear reductive elimination of $CpW(CO)_3Me$ (0.02 M in benzene) were made by monitoring the band maximum at 508 nm of the product complex $Cp_2W_2(CO)_6$ with a Beckman DU spectrophotometer. The light source for irradiations was a 200-W Oriel high-pressure mercury lamp. Intensities were varied with use of Oriel neutral-density filters. Each value was based on three independent sets of three consecutive irradiations. Substitution quantum yields were determined by monitoring the 2016- and 1918-cm^{-1} bands of $CpW(CO)_3Me$ and the 1933- and 1847-cm^{-1} bands of $CpW(CO)_2(PPh_3)Me$ with a Perkin-Elmer 983 spectrophotometer. Lamp intensities were measured by ferrioxalate actinometry. The 366- and 405-nm mercury arc bands were isolated with use of a Corning CS 7-83 filter and an Edmund Scientific interference filter, respectively. $CpW(CO)_3Me$ was prepared by literature methods.[7] All other materials were obtained commercially. Benzene was distilled under nitrogen from $LiAlH_4$.

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Appendix

The observed quantum yield for the reaction in Scheme I will be dependent on the competition between the forward reaction and the back-reaction, the latter of which is dependent on the steady-state concentration of M. The quantum yield at any given point X in solution will be

$$\phi_X = \phi_p k_2[\text{RHal}]/(2k_{-1}[\text{M}]_X + k_2[\text{RHal}]) \qquad (10)$$

where ϕ_p is the quantum yield for the primary photoprocess (metal–metal bond homolysis) and $[\text{M}]_X$ is the steady state concentration of [M] at point X. Let us assume a rectangular-prism reaction cell of pathlength L, evenly irradiated over all or part of one surface, with the incident light, perpendicular to the irradiated surface, distributed over area A. Let x equal the distance of point X from the irradiated surface, ϵ equal the extinction coefficient of M–M at the wavelength of irradiation, I_0 equal the incident radiation intensity, and C equal the concentration of M–M. Using the steady-state approximation for M, we then find

$$[\text{M}]_X = \frac{b + (b^2 + 8k_{-1}f)^{1/2}}{4k_{-1}} \qquad (11)$$

where

$$b = -k_2[\text{RHal}] \qquad (12)$$

$$f = (2\phi_p I_0 \epsilon C(\ln 10)10^{-\epsilon Cx})/(A/1000) \qquad (13)$$

The value for the overall quantum yield ϕ_t can be obtained by integration over the length of the cell (from $x = 0$ to L):

$$\phi_t = \frac{(\ln 10)\epsilon C}{(1 - T)} \int_{x=0}^{x=L} \frac{\phi_x I_x}{I_0}\,dx \qquad (14)$$

where $I_x = I_0 10^{-\epsilon Cx}$ is the intensity at point x. Making the substitution $u = 10^{-\epsilon Cx}$ and integrating, we find

$$\phi_t = \frac{2b\phi_p}{(1 - T)}\left[\frac{-(\ln 10)b\epsilon CL}{z} + \frac{2}{z}(b^2 - zT)^{1/2} - \frac{2}{z}(b^2 - z)^{1/2} + \frac{b}{z}\ln\left(\frac{(b^2 - zT)^{1/2} - b}{(b^2 - zT)^{1/2} + b}\right) - \frac{b}{z}\ln\left(\frac{(b^2 - z)^{1/2} - b}{(b^2 - z)^{1/2} + b}\right)\right] \qquad (3)$$

where T is the transmittance of the solution ($10^{-\epsilon CL}$) and $z = -16k_{-1}\phi_p I_0 \epsilon C(\ln 10)/(A/1000)$.

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $Mn(CO)_5$, 14971-26-7; $CpW(CO)_3Me$, 12082-27-8; $Cp_2W_2(CO)_6$, 12091-65-5; $CpW(CO)_2(PPh_3)Me$, 12115-41-2.

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(7) See ref 4b, Experimental Section, and references therein.

Contribution from the Department of Chemistry,
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Kinetics of the Ligand Substitution Reactions of a Labilized Chromium(III) Complex, $[(NH_3)_5Co\{(edta)Cr(H_2O)\}]^{2+}$

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The EDTA and related polyamino polycarboxylate ligands have been shown to labilize greatly the ligand substitution reactions of the chromium(III) complexes.[1] Later, trivalent metal complexes other than those of chromium(III), including titanium(III), iron(III), cobalt(III), ruthenium(III), and osmium(III) complexes, were also found to undergo rapid ligand substitution reactions when an EDTA-type ligand was coordinated.[2–6] This remarkable effect of the EDTA-type ligand has attracted continuing attention for a decade.[7]

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(7) Abbreviations used in this note: EDTA, ethylenediamine-*N,N,N′,N′*-tetraacetate; HEDTRA, *N*-(hydroxyethyl)ethylenediamine-*N,N′,N′*-triacetate; OAc$^-$, acetate.

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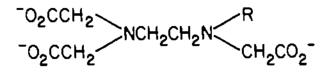
The mechanism for such labilization of the chromium(III) complexes was discussed in relation to the structure of the Cr(III)–EDTA complex in solution.[1,4,6] Our proposal is that transient coordination of the R group in the polyamino polycarboxylate ligand **1** to the chromium(III) center is attributed to the rapid

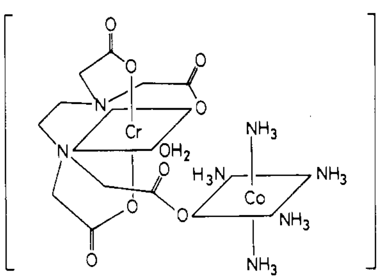


$(^-O_2CCH_2)_2NCH_2CH_2N(R)CH_2CO_2^-$

1

ligand substitution, where R represents $CH_2CO_2^-$, CH_2COOH, CH_2CH_2OH, or $CH_2CH_2OC(O)CH_3$. This account is based on the quinquedentate structure of the coordinated polyamino polycarboxylate ligand **1**, although there is dispute over the solution structure of the Cr(III)–EDTA complex.[6,8,9]

The lability of the chromium(III) center will be controlled by such factors as nucleophilicity of the pendant R group, overall charge of the complex, and the bulkiness of the R group. Therefore, wide variation of the R group should merit study to elucidate the role of the polyamino polycarboxylate ligand. In this regard, we have examined the kinetics of the ligand substitution reactions (eq 1) of $[(NH_3)_5Co\{(edta)Cr(H_2O)\}]^{2+}$ (**2**)[10] in which one of the CH_2COO^- groups of the $edta^{4-}$ ligand is bound to the $Co(NH_3)_5^{3+}$ moiety, i.e. R = $CH_2C(O)OCo(NH_3)_5$.



2

$$[(NH_3)_5Co\{(edta)Cr(H_2O)\}]^{2+} + X^- \xrightleftharpoons[k_{aq}]{k_{an}} [(NH_3)_5Co\{(edta)CrX\}]^+ + H_2O \quad (1)$$

$$X^- = OAc^-, N_3^-, NCS^-$$

Experimental Section

The perchlorate salt of **2** was prepared according to the literature.[10] Kinetic measurements were made at I = 1.0 ($NaClO_4$) and 25.0 °C under pseudo-first-order conditions. The reaction was monitored spectrophotometrically by using a Union Giken RA-401 stopped-flow spectrophotometer. The hydrogen ion concentrations were controlled with HOAc–NaOAc buffer solutions for the reaction with OAc^-, with perchloric acid for the reaction with NCS^-, and with HN_3–NaN_3 buffer solutions for the reaction with N_3^-, respectively, and were measured with a Toa HM-20B pH meter. The reactions followed a pseudo-first-order rate law.

Results and Discussion

The observed pseudo-first-order rate constants (k_{obsd}) followed the rate equation (2) for the reactions with NCS^- and N_3^-, where

$$k_{obsd} = k_{an}[X^-] + k_{aq} \quad (2)$$

k_{an} and k_{aq} are the rate constants of the anation and the aquation reactions of eq 1, respectively. The k_{an} and k_{aq} values were acid-independent at $[H^+] = 1.5 \times 10^{-4}$–$1.3 \times 10^{-2}$ M for the reaction with NCS^- and at $[H^+] = 3.5 \times 10^{-6}$–$1.2 \times 10^{-4}$ M for the reaction with N_3^-. On the other hand, the k_{obsd} values of the reaction with OAc^- were found to be acid-dependent at $[H^+] = 5.9 \times 10^{-6}$–$6.4 \times 10^{-5}$ M in a manner similar to the reaction of $[Cr(edta)(H_2O)]^-$ with OAc^-.[1] In the $[Cr(edta)(H_2O)]^-$–OAc^- reaction, both OAc^- and HOAc are the reactive species to replace the coordinated water molecule.[1,4] Therefore, the reaction of **2** was analyzed by reactions 3–5, which lead to the rate equation (6), where k_{an}, k'_{an}, k_{aq}, and k'_{aq} are the relevant rate constants

$$[(NH_3)_5Co\{(edta)Cr(H_2O)\}]^{2+} + OAc^- \xrightleftharpoons[k_{aq}]{k_{an}} [(NH_3)_5Co\{(edta)Cr(OAc)\}]^+ + H_2O \quad (3)$$

$$[(NH_3)_5Co\{(edta)Cr(H_2O)\}]^{2+} + HOAc \xrightleftharpoons[k'_{aq}]{k'_{an}} [(NH_3)_5Co\{(edta)Cr(OAc)\}]^+ + H_3O^+ \quad (4)$$

$$[(NH_3)_5Co\{(edta)Cr(H_2O)\}]^{2+} \xrightleftharpoons{K_a} [(NH_3)_5Co\{(edta)Cr(OH)\}]^+ + H^+ \quad (5)$$

$$k_{obsd} = \frac{k_{an} + k'_{an}K_{HOAc}^{-1}[H^+]}{1 + K_a[H^+]^{-1}}[OAc^-] + k_{aq} + k'_{aq}[H^+] \quad (6)$$

given in reactions 3 and 4. K_{HOAc} denotes the acid dissociation constant of acetic acid, and K_a ($=1.41 \times 10^{-6}$ M), the acid dissociation constant of the H_2O ligand in **2**.

Table I. Anation Rate Constants ($k_{an}/M^{-1}\ s^{-1}$) for the Reaction of $[CrL(H_2O)]^{(n-3)-}$ with Anions (X^-)[a]

	X^-		
$[CrL(H_2O)]^{(n-3)-}$	OAc^-	N_3^-	NCS^-
2	44.5 ± 1.1[b]	676 ± 15[b]	133 ± 1[b]
$[Cr(edta)(H_2O)]^-$	3.3 ± 0.4[c]	98 ± 5[d]	13.7 ± 0.6[e]
$[Cr(hedtra)(H_2O)]$	7.60 ± 0.61[c]	19.8 ± 1.2[e]	3.32 ± 0.11[e]

[a] I = 1.0 ($NaClO_4$), 25.0 °C. [b] This work. [c] Reference 1. [d] Reference 11. [e] Reference 4.

Table II. Aquation Rate Constants (k_{aq}/s^{-1}) of $[CrXL]^{(n-2)-}$[a]

	X^-		
$[CrXL]^{(n-2)-}$	OAc^-	N_3^-	NCS^-
2	2.1 ± 0.4[b]	7.25 ± 0.08[b]	4.2 ± 0.1[b]
$[CrX(edta)]^{2-}$	5.4 ± 0.6[c]	13.4[d]	26.8 ± 1.9[e]
$[CrX(hedtra)]^-$	0.450 ± 0.030[c]	0.189 ± 0.012[e]	0.244 ± 0.019[e]

[a] I = 1.0 ($NaClO_4$), 25.0 °C. [b] This work. [c] Reference 1. [d] Reference 11. [e] Reference 4.

Table III. Formation Constants (K/M^{-1}) of $[CrXL]^{(n-2)-}$ for the Reaction of $[CrL(H_2O)]^{(n-3)-}$ with Anions (X^-)[a]

	X^-		
$[CrL(H_2O)]^{(n-3)-}$	OAc^-	N_3^-	NCS^-
2	21 ± 4[b]	93.2 ± 3.1[b]	32 ± 1[b]
$[Cr(edta)(H_2O)]^-$	0.62 ± 0.03[c]	5.9 ± 0.3[c]	0.57 ± 0.07[d]
$[Cr(hedtra)(H_2O)]$	16.9 ± 0.9[c]	110 ± 15[d]	13.6 ± 1.2[d]

[a] I = 1.0 ($NaClO_4$), 25 °C. [b] This work. [c] Reference 1. [d] Reference 4.

The k_{an} and k_{aq} values are summarized in Tables I and II. k'_{an} and k'_{aq} for the reaction with OAc^- were determined to be $k'_{an} = 13.3 \pm 1.3\ M^{-1}\ s^{-1}$ and $k'_{aq} \leq 8 \times 10^3\ M^{-1}\ s^{-1}$. The equilibrium constants (K) for reaction 1, which were determined by eq 7, are listed in Table III.

$$K = k_{an}/k_{aq} \quad (7)$$

The substitutions of the coordinated water molecule in **2** with OAc^-, N_3^-, and NCS^- proceed 10^6–10^8 times faster than the corresponding reactions of $[Cr(H_2O)_6]^{3+}$ and $[Cr(NH_3)_5(H_2O)]^{3+}$ complexes. To our knowledge, the anation reaction of **2** with N_3^- is the fastest among the ligand substitution reactions of chromium(III) complexes so far studied.

The 15-fold difference in k_{an} values between the N_3^- and OAc^- reactions may support an associative attack of the entering ligand. Apparently, larger size of the pendant group (i.e. $Co(NH_3)_5^{3+}$ moiety) does not sterically prevent the entering ligand from approaching the chromium(III) center, although unfavorable steric

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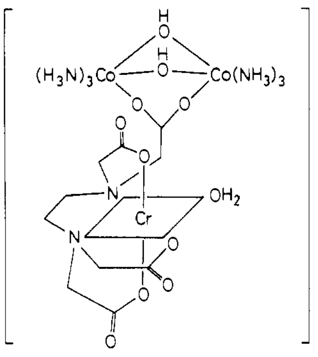
factors may be canceled out by the positively charged $Co(NH_3)_5^{3+}$ moiety for the uninegative entering ligand to approach. Also, incorporation of OAc^-, N_3^-, and NCS^- is thermodynamically not unfavorable compared to the case of EDTA and HEDTRA complexes.

Recently complex **3** was prepared, and the slow ligand substitution reactions with OAc^- and NCS^- were demonstrated.[12]



3

Comparing this result with the reactivity of **2**, we conclude that a carboxylate or a carbonyl oxygen atom in the pendant group must remain free for the labilization of the chromium(III) center.

The $[H^+]$ dependence of the rate of the reaction of **2** with OAc^- can be compared with that of the reaction of the Cr(III)-EDTA complex with OAc^-. In the case of **2**, reactions are clearly formulated as eq 3 and 4, and there is no so-called proton ambiguity encountered in the reaction of the Cr(III)-EDTA complex.[1,4] k'_{an} is of the same order of magnitude as k_{an}, and this trend is the same as for the Cr(III)-EDTA reaction.

In conclusion, the reactions of **2** have shown that the contribution of the steric factor of the pendant group is surprisingly small and the nucleophilic assistance of the ligand substitution by the pendant group is more important.

Registry No. $[(NH_3)_5Co\{(edta)Cr(H_2O)\}]^{2+}$, 61813-16-9; OAc^-, 71-50-1; N_3^-, 14343-69-2; NCS^-, 302-04-5.

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Reactions of Coordinated Molecules. 45. Identification of Another Isomer of (Ferra β-diketonato)difluoroboron Complexes

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During our study of the chemistry of metalla β-diketones and their corresponding enolate anions, we isolated a class of neutral (metalla β-diketonato)B(X)(Y) complexes in which the metalla β-diketonate anion coordinates as a bidentate, chelating ligand to the boron atom.[2-4] Solution infrared spectral data of the (ferra β-diketonato)difluoroboron complexes, $[(\eta\text{-}C_5H_5)(OC)Fe(RCO)(R'CO)]BF_2$, indicated the presence of two isomers in solution.[4] One isomer exhibits a carbonyl stretching band in the range 1960-1975 cm^{-1}, while the other isomer shows a carbonyl stretching band in the region 2000-2020 cm^{-1}. The relative amounts of these isomers (which undergo interconversion) are affected by changes in solvent polarity.

A structural determination of a (ferra β-diketonato)BF_2 complex in which R = Me and R′ = *i*-Pr revealed a boat-shaped conformation for the ferra chelate ring.[5] The carbonyl ligand now occupies the axial position at the Fe atom in greatest proximity to the axial fluorine substituent at the boron atom. The C_5H_5 ligand occupies an equatorial site at the Fe atom. For this isomer, the carbonyl C-O stretching frequency is observed at 2005 cm^{-1} in KBr. The structure of the second isomer (which has the lower C-O stretching frequency) was assumed to be the alternate boat isomer having an axial C_5H_5 substituent at the Fe atom, although the possibility of a chair conformation for this isomer could not be excluded.

We now report the preparation and structural characterization of the complex $[(\eta\text{-}C_5H_5)(OC)Fe(Me_3CCO)_2]BF_2$. This complex has a single C-O stretching band in solution at 1962 cm^{-1} and in the solid state (KBr) at 1956 cm^{-1}. The molecular structure reveals a boat-shaped conformation for the ferra chelate ring in which the C_5H_5 ligand now occupies the axial position. This observation unambiguously establishes the identity of the second geometrical isomer of this class of compound. The two boat isomers apparently interconvert by a "flipping" of the Fe and B atoms through an excited state having a planar six-membered ring. Structural characterization of the solution and solid-state conformations of (ferra β-diketonato)BF_2 complexes is relevant to a more complete understanding of the interligand C-C coupling reactions and Diels-Alder cycloaddition chemistry of these molecules.[6-10]

Experimental Section

All preparative chemistry was performed with standard inert-atmosphere techniques and solvent preparation as specified elsewhere.[4] Infrared and ^1H NMR spectra were obtained also as reported earlier.[4] Microanalysis was performed either by Galbraith Laboratories or by MicAnal Ltd.

Preparation of $(\eta\text{-}C_5H_5)(OC)_2FeC(O)CMe_3$ (1). Complex **1** was prepared according to a procedure similar to that used to prepare $(\eta\text{-}C_5H_5)(OC)_2FeC(O)CHMe_2$[11] and was isolated as amber crystals (61%): mp 70.5-71.5 °C; IR (C_6H_{12}) ν(CO) 2005 (s), 1960 (s) cm^{-1}; ^1H NMR $(CDCl_3)$ δ 1.08 (s, 9, Me_3C), 4.90 (s, 5, C_5H_5). Anal. Calcd for $C_{12}H_{14}FeO_3$: C, 55.00; H, 5.38. Found: C, 55.01; H, 5.49.

Preparation of $[(\eta\text{-}C_5H_5)(OC)Fe(Me_3CCO)_2]BF_2$ (2). To a stirred amber solution of 4.20 g (11.35 mmol) of **1** in 170 mL of ether at -78 °C was added dropwise 8.36 mL of a 1.9 M solution of *tert*-butyllithium over a 5-min period. The reaction solution was warmed to ca. -20 °C over a 30-min period, during which time the color changed to orange-brown. The solvent was removed at reduced pressure. The residue was dissolved in 150 mL of CH_2Cl_2, and then this solution was cooled to -78 °C. Boron trifluoride gas was bubbled through this solution at a moderate rate for 2 min. The reaction mixture was then warmed to room temperature. The solvent was removed at reduced pressure, and the residue was chromatographed on a Florisil/ether column. Crystallization from ether solution afforded 4.09 g (71%) of **2** as orange crystals: mp 140-142 °C; IR (hexane) ν(CO) 1962 cm^{-1}; ^1H NMR $(CDCl_3)$ δ 1.17 (s, 18, Me_3C), 4.76 (s, 5, C_5H_5). Anal. Calcd for $C_{16}H_{23}BF_2FeO_3$: C, 52.21; H, 6.32. Found: C, 51.94; H, 6.15.

X-ray Crystallographic Measurements. Amber crystals of **2** were obtained by crystallization from ether/pentane solution at -20 °C. Precession photography indicated $2/m$ Laue symmetry and systematic absences appropriate for the space group $P2_1/c$. Most parameters pertaining to data collection and structure solution and refinement are listed in Table I. Intensity data were collected on a four-circle automated

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