yielding μ-H[$W_2(CO)_9PPh_3$]$^-$, whereas μ-H[$Cr_2(CO)_{10}$]$^-$ in the presence of PPh_3 leads to the production of $Cr(CO)_4[PPh_3]_2$ upon either thermal or photochemical activation.

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Registry No. [Et_4N][$HCr_2(CO)_{10}$], 16924-36-0; [Et_4N][$HW_2(CO)_{10}$], 12083-01-1; K[$HCr_2(CO)_{10}$], 61453-56-3; $W(CO)_5THF$, 36477-75-5; μ-H[$W(CO)_5$][$W(CO)_4(^{13}CO)$]$^-$, 68212-99-7; μ-H[$Cr(CO)_5$][$Cr(CO)_4(^{13}CO)$]$^-$, 68212-92-0; [Et_4N][$HW_2(CO)_9PPh_3$], 68212-91-9; $Cr(CO)_5PPh_3$, 14917-12-5; $Cr(CO)_4(PPh_3)_2$, 42029-71-0.

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Intramolecular Associative Assistance in the Labilization of Chromium(III) Complexes: A Comparison of the Acid Aquation of 2,4-Pentanedione from Cr(hedta)(acac)$^-$ and Cr(edda)(acac)

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The H_3O^+-assisted aquation of Hacac from Cr(hedta)(acac)$^-$ and Cr(edda)(acac) has been studied. An accelerated rate of about 10^3 relative to normal dissociative paths of Cr(III) complexes is observed for the Cr(hedta)(acac)$^-$ case. The pendant group effect for labilizing Cr(III), as proposed by Ogino and by Sykes, is proposed to account for the 10^3 enhancement. H_3O^+ scavenging of the distorted intermediates produced by pendant group association at Cr(III) is found to be much more rapid than the reverse reaction to the ground state. The Cr(hedta)(acac)$^-$ aquation occurs via two pendant arm-assisted pathways: (A) for Cr(hedtaH)(acac) and (B) for Cr(hedta)(acac)$^-$. The following kinetic parameters are obtained at μ = 0.20 ($NaClO_4$): $\Delta H_A^\ddagger$ = 21.34 ± 1.30 kcal/mol, $\Delta S_A^\ddagger$ = −0.89 ± 1.15 eu; $\Delta H_B^\ddagger$ = 16.68 ± 2.50 kcal/mol, $\Delta S_B^\ddagger$ = −21.39 ± 8.20 eu. The relative rates to achieve the distorted intermediates (k_2/k_1) is 51 in favor of assistance from the anionic carboxylate, the (B) path. The association constant for formation of Cr(hedta)(acac)$^-$ from Cr(hedta)(H_2O) and acac$^-$ was evaluated by competition with H_3O^+ to be (5.87 ± 0.24) × 10^5 M^{-1} (μ = 0.20, T = 25.0 °C). Bidentate acac$^-$ exhibits the normal chelate effect on the stability constant relative to monodentate anions, X$^-$, of ca. 2.9 × 10^4. The acid aquation of Cr(edda)(acac) proceeds by the normal dissociative pathway, scavenged by H_3O^+, in competition with return of the distorted intermediate to the ground state. At μ = 1.00 ($NaClO_4$), 25.0 °C, k_5 = 2.99 × 10^{-5} s^{-1} for the distortion step with k_{-5}/k_6, reversion to ground state vs. H_3O^+ scavenging, of 0.19. Comparisons are made to previous studies concerning the acid aquation of $Cr(acac)_3$.

Introduction

Cr(III) complexes having approximately octahedral environments are generally found to be of the substitution inert class. This is consistent with the large ligand field stabilization of the t_{2g}^3 configuration and the high activation enthalpy for a dissociative path which leads to ligand or solvent exchange. Ligand substitution at Cr(III) is moderately accelerated by oxyanions (SO_3^{2-},[1-3] NO_3^-,[4] NO_2^-,[5,6] carboxylates (RCO_2^-)[7,8]). The catalysis for the oxyanions for replacement of H_2O by entering nucleophiles, X$^-$, has been interpreted on the basis of anchimeric assistance provided by chelation of the oxyanion in the transition state.[2,3,7,8] Addition of X$^-$ to $CrY(H_2O)^{n-}$ (X$^-$ = $CH_3CO_2^-$, N_3^-, CrO_4H^-, MoO_4H^-, WO_4H^-; Y = hedta^{3-} or edta^{4-}) is observed to be much more rapid than the addition of X$^-$ to complexes such as $Cr(CH_3CO_2)(H_2O)_5^{2+}$ where the anchimeric effect is manifest.[9,10] Anation of $CrY(H_2O)^{n-}$ by X$^-$ is in the stopped-flow range. Addition of X$^-$ to $CrY(H_2O)^{n-}$ proceeds with apparent second-order rate constants ca. 10^3 larger than anation rates of $Cr(H_2O)_6^{3+}$ or $Cr(CH_3CO_2)(H_2O)_5^{2+}$.

The aminocarboxylate ligands have donor groups similar to the more common amino acid residues. Chromium may be assimilated by biological organisms from sources of environmental contamination (fly-ash, vegetable sources, mine

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leaching waters, paints, etc.). If chromium is brought to equilibrium as Cr(III) with biopolymers, the $CrY(H_2O)^{n-}$ substitution rates establish the possibility that Cr(III) substitution may occur on a time scale which is competitive with biochemical substrate turnovers and synthesis. Therefore the factors which promote the enhancement of ligand substitution at Cr(III) in aminocarboxylate environments have a physiological significance. Ogino[9] and Sykes[10] have suggested that the addition of a free $-CH_2COOH$, $-CH_2COO^-$, or $-CH_2CH_2OH$ in an associative intramolecular step is responsible for the kinetic lability of $CrY(H_2O)^{n-}$ complexes for the addition of monodentate X^- donors. We report here a similar pendant group assistance for the acid aquation of the 2,4-pentanedionato chelate ligand ($acac^-$) from Cr(hedta)-$(acac)^-$. The comparison study of Cr(edda)(acac) in which the first coordination sphere contains a virtually identical primary interaction of the chelating ligands toward Cr(III) has been made to assist the interpretation. The mechanism for the loss of Hacac from Cr(III) complexes is discussed in terms of distorted intermediates in which a Cr–O bond is partially ruptured in the transition state.

Experimental Section

Cr(hedta)(acac)$^-$ Solutions. Solutions containing Cr(hedta)(H_2O) were prepared by stoichiometric mixing of $[Cr(H_2O)_6](ClO_4)_3$ and H_3hedta with 3 equiv of NaOH in H_2O. The solution pH was adjusted to 5.45 and the aqueous solutions were heated at 50 °C for 24 h. Typical stock solutions containing 3.46×10^{-3} M Cr(hedta)(H_2O) were prepared. Cr(hedta)$(acac)^-$ solutions for kinetic work were generated from aliquots of Cr(hedta)(H_2O) and Hacac. Usually a sample containing a 7:1 [Hacac]:[Cr(III)] ratio was adjusted to pH 7.50 in μ = 0.20 $NaClO_4$ to induce complete formation of Cr-$(hedta)(acac)^-$. The solutions were allowed to stand overnight to ensure complete conversion to Cr(hedta)$(acac)^-$ at room temperature.

[Cr(edda)(acac)]·2H_2O. The crystalline product was prepared by a modification of the procedure of Fuji.[11] A 5.28-g sample of $CrCl_3 \cdot 3H_2O$ and 8.00 g of H_2edda were heated in 40 mL of H_2O after adjustment to pH 3–4 with $(NH_4)_2CO_3$. Hacac (2.00 g) was added and the pH was readjusted to 7 with $(NH_4)_2CO_3$. The solution was chilled in the refrigerator overnight and placed in an ice/salt slush (−10 °C) to induce crystallization. The filtered crystals were recrystallized from 20 mL of 50% CH_3OH/50% H_2O. The product was recovered from CH_3OH/H_2O upon chilling in a refrigerator (4 °C). Cr(edda)(acac) exhibits maxima at 380 nm (ϵ 168 M^{-1} cm^{-1}) and 532 nm (ϵ 65 M^{-1} cm^{-1}) in aqueous solution.

Spectral and Kinetic Measurements. Electronic spectra were obtained using a Varian-Cary 118 C spectrophotometer with a thermostated sample compartment. The temperature was controlled to ±0.03 °C with a Forma circulator bath. Aquation kinetic experiments were monitored at 350 nm for Cr(hedta)$(acac)^-$ studies and 380 nm for Cr(edda)(acac) using either the Cary 118C unit or a Durrum D-110 stopped-flow device. First-order plots of ln $(A_\infty - A)$ vs. time were used to evaluate pseudo-first-order reactions. Least-squares treatment of the kinetic data and standard deviations were calculated using a Declab 1103 computer with appropriate Fortran programs. Data analysis was off-line for Cary runs and on-line for stopped-flow studies. Infrared spectra were obtained in KBr pellets on a Beckman Acculab 4 instrument. Temperature preequilibrated samples of the CrL(acac) and H_3O^+ solutions were rapidly mixed between glass vessels. The sample solutions were exposed to the atmosphere. The mixed solutions were quickly transferred to temperature-equilibrated 1.00-, 5.00-, or 10.00-cm cells and placed in the spectrophotometric block for the slow kinetic runs.

Hydrogen Ion Concentrations. Hydrogen ion solution concentrations were obtained by calculation from the dilution of titrated standard solutions for the pH domain where the proton saturation of the glass electrode is a problem. Weaker solutions were measured using an Orion 701 digital pH meter calibrated against commercial buffers. Readings were appropriately corrected for ionic strength variations in different media.

Results and Discussion

Cr(hedta)(acac)$^-$ System. The Cr(hedta)$(acac)^-$ complex is obtained by replacement of two coordination positions of

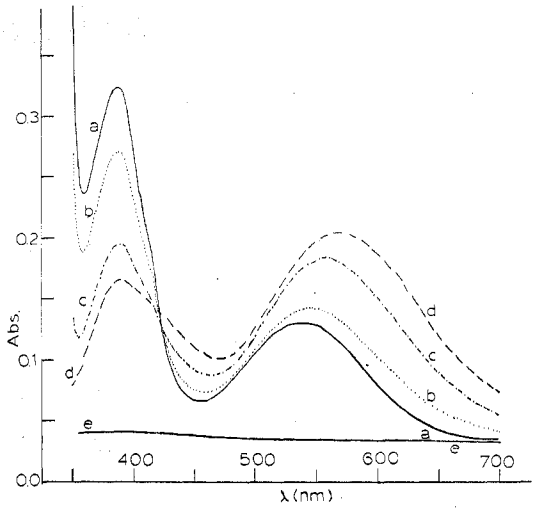


Figure 1. Visible spectra (at 25.0 °C, μ = 0.20, pH 7.50): (a) —, limiting spectrum of Cr(hedta)$(acac)^-$, [Cr(III)]:[Hacac] = 1:50; (b) ···, spectrum for [Cr(III)]:[Hacac] = 1:5.0; (c) ·-·, spectrum for [Cr(III)]:[Hacac] = 1.0:1.0; (d) ---, spectrum for Cr(hedta)-$(OH)^-$/Cr(hedta)(H_2O); (e) lower solid line, baseline. $[Cr(III)]_{tot}$ = 1.137×10^{-3} M in all spectra.

Cr(hedta)(H_2O); one glycinato chelate ring is broken at the expense of formation of one 2,4-pentanedionato ring in the mixed chelate complex (eq 1). The resultant pendant

$$Cr(hedta)(H_2O) + Hacac \overset{K_1}{\rightleftharpoons} Cr(hedta)(acac)^- + H_3O^+ \quad (1)$$

carboxylate is available for protonation (eq 2). The pK_a of

$$Cr(hedta)(acac)^- + H_3O^+ \overset{1/K_a}{\rightleftharpoons} Cr(hedtaH)(acac) + H_2O \quad (2)$$

$$H_3O^+ + acac^- \overset{1/K_a'}{\rightleftharpoons} Hacac \quad (3)$$

the pendant carboxylate moiety in Cr(edta)$(H_2O)^-$ is 1.8 ± 0.2 (μ = 0.10, 25 °C).[9] The pK_a for Cr(edtaH)(H_2O) should serve as a close estimate for the pK_a of Cr(hedtaH)(acac) since the charge repulsion distances between H^+ and Cr(III) are equal and the remaining charge environment and solvation shell are very similar. The pK_a for 2,4-pentanedione is 8.85 (eq 3). Equilibria (1), (3), and (4) are interrelated by $K_f = K_1/K_a'$; K_a' is the acid dissociation constant of 2,4-pentanedione (Hacac). The value of K_f (eq 4) would be useful to compare

$$Cr(hedta)(H_2O) + acac^- \overset{K_f}{\rightleftharpoons} Cr(hedta)(acac)^- + H_2O \quad (4)$$

$$Cr(hedta)(H_2O) + X^- \overset{K_x}{\rightleftharpoons} Cr(hedta)X^- + H_2O \quad (5)$$

to values of K_x from anation studies ($X^- = N_3^-$, $CH_3CO_2^-$, and MO_4H^- species[9,10]) where X^- is monodentate compared to the bidentate $acac^-$. At pH 7.50, μ = 0.20 ($NaClO_4$), the spectrum of Cr(hedta)$(OH)^-$ undergoes alterations on addition of Hacac. A limiting spectrum of Cr(hedta)$(acac)^-$ is obtained if $\{[Hacac]/[Cr(III)]\}_{tot} \geq 10$. Banerjea and Chaudhuri have studied the displacement of $acac^-$ by $edtaH^{3-}$ in $Cr(acac)_3$.[12] Their study indicated no mixed Cr(edta)$(acac)^{2-}$ product but only the Cr(edta)(H_2O)/Cr(edta)$(OH)^{2-}$ equilibrium. Their report is consistent with our observation; the final equilibrium state in Banerjea's experiments would have $[acac^-]/[Cr(edta)(OH)^{2-}]$ = 3.0 at the elevated temperature of 80 °C compared to the results we report here for the neutrally charged Cr(hedta) center at 25.0 °C. Warming of the

Table I. Dissociation of Cr(hedta)(acac)$^-$ Suppressed by Additional Hacac[a]

$[Hacac]_i/[Cr(hedta)(acac)^-]^b = n$	$\lambda_{max}{}^1$,[c] nm	$\lambda_{max}{}^2$,[c] nm	$10^3 k_{obsd}$, s^{-1}
0.00	387.5	563.0	2.31 ± 0.01
2.00	389.0	555.0	2.42 ± 0.04
4.00	388.0	552.0	2.66 ± 0.03
6.00	387.5	548.0	2.71 ± 0.01
9.00	387.5	548.0	2.72 ± 0.01
24.0	386.0	540.0	2.69 ± 0.01
49.0	384.0	540.0	2.65 ± 0.03
99.0	384.0	537.0	2.52 ± 0.01
262.0			2.09 ± 0.01

[a] $[Cr(hedta)(acac)^-]_i = 8.55 \times 10^{-4}$ M, $\mu = 0.20$ ($NaClO_4$), $T = 25.0$ °C, pH 1.40. [b] $[Hacac]_f = (n + 1.00)[Cr(hedta)(acac)^-]_i$. [c] Weighed average of spectral positions for Cr(hedta)(H_2O) or Cr(hedta)(acac)$^-$ as a function of added Hacac.

equilibrium mixture of Cr(hedta)(acac)$^-$ and Cr(hedta)(OH)$^-$ at pH 7.8 shifts the equilibrium of eq 6 to the right: the blue

$$\underset{\text{purple}}{Cr(hedta)(acac)^-} + OH^- \rightleftharpoons \underset{\text{blue}}{Cr(hedta)(OH)^-} + acac^- \quad (6)$$

Cr(hedta)(OH)$^-$ is favored at 60 °C while the purple Cr(hedta)(acac)$^-$ is dominant at 25.0 °C. Between pH 7 and 8 the equilibration time to achieve total formation of Cr(hedta)(acac)$^-$ depends on $\{[Hacac]/[Cr(III)]\}_{tot}$. The process is complete in ca. 3 h at room temperature with $\{[Hacac]/[Cr(III)]\}_{tot} = 7.0$. The spectrum of Cr(hedta)(acac)$^-$ is shown in Figure 1. Maxima occur at 538 nm (ϵ 85.3) and 387 nm (ϵ 253) which are the anticipated $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions in a pseudooctahedral ligand field for Cr(III).

Kinetics of Hacac Removal from Cr(hedta)(acac)$^-$. The acid-promoted conversion of Cr(hedta)(acac)$^-$ to Cr(hedta)(H_2O) was monitored at λ 350 nm for the range $1.2 \leq$ pH ≤ 1.80. At high concentrations of free Hacac the reaction did not proceed to completion as suggested for the forward step of eq 1. The rate of approach to the final equilibrium was studied as a function of [Hacac]. The data are presented in Table I. The reverse reaction for re-formation of Cr(hedta)(acac)$^-$ was found to be a kinetically neglectable effect if $\{[Hacac]/[Cr(III)]\}_{tot} \leq 25$. Kinetic studies for the acid-promoted dissociation were conducted with $[Hacac]/[Cr(III)] = 7.0$ in order to ensure complete initial formation of Cr(hedta)(acac)$^-$ in the synthetic step but in a range of concentration ratios of $\{[Hacac]/[Cr(III)]\}_{tot}$ where the reverse kinetic steps dependent on [Hacac] were noncompetitive. The acid aquation of Hacac was studied as a function of $[H_3O^+]$ at various temperatures (Table II). The kinetic data conform to the rate expression given by eq 7. The temperature de-

$$\frac{d[Cr(hedta)(H_2O)]}{dt} = \left\{A + \frac{B}{[H_3O^+]}\right\}[Cr(hedta)(acac)]_{tot} \quad (7)$$

pendence for coefficients A and B of k_{obsd} are given in Table III. The Eyring rate dependence of the A and B paths are shown in Figure 2. The activation parameters associated with these paths are as follows: A path, $\Delta H^\ddagger = 21.34 \pm 1.30$ kcal/mol, $\Delta S^\ddagger = -0.89 \pm 1.15$ eu; B path, $\Delta H^\ddagger = 16.68 \pm 2.50$ kcal/mol, $\Delta S^\ddagger = -21.39 \pm 8.20$ eu. The simplest mechanism which accounts for an acid-independent term (A) and an inverse acid term (B) over the range in $[H_3O^+]$ where both

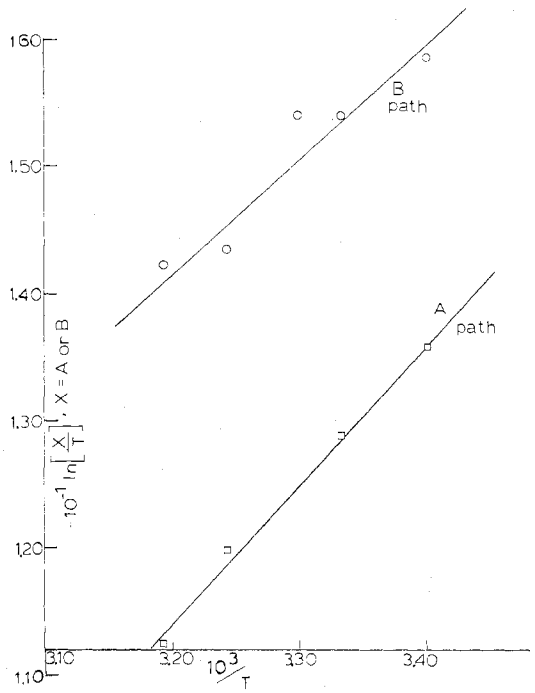


Figure 2. Eyring temperature dependence for the A and B acid aquation paths of Cr(hedta)(acac)$^-$; conditions are as given in Table III.

Table II. Temperature Dependence of the H_3O^+-Promoted Aquation of Cr(hedta)(acac)$^-$ [a]

$10^2[H_3O^+]$, M	$10^1(1/[H_3O^+])$, M^{-1}	10^3k,[b] s^{-1} 20.9 °C	26.0 °C	30.0 °C	35.2 °C	40.0 °C
6.31	1.58			1.78	4.01	6.27
5.01	2.00			1.87	5.96	8.22
3.98	2.51		2.38	2.26	6.82	9.81
3.16	3.16	1.65	2.72	2.69	7.62	12.0
2.51	3.98	1.88	3.15	2.94	9.67	12.3
2.00	5.01	2.27	3.79	4.19	11.1	14.4
1.58	6.31	2.81	4.89	4.89	13.1	17.0
1.26	7.94	3.46	5.62			

[a] $[Cr(III)]_i = 9.10 \times 10^{-4}$ M, $[Hacac]_i = (4.99\text{–}6.37) \times 10^{-3}$ M, $\mu = 0.20$ ($NaClO_4$). [b] Error estimate to ±0.01 in recorded value.

Table III. Temperature Dependence of A and B Pathways for Aquation of Cr(hedta)(acac)$^-$, $\mu = 0.20$[a]

T, °C	$10^3/T$, K^{-1}	10^3A, s^{-1}	$-\ln((A/T) \times 10^{-1})$	10^4B, M s^{-1}	$-\ln((B/T) \times 10^{-1})$
20.9	3.401	0.377 ± 0.062	1.357	0.385 ± 0.011	1.585
26.0	3.343	0.765 ± 0.142	1.288	0.621 ± 0.028	1.539
30.0	3.299	0.541 ± 0.175	1.324	0.686 ± 0.456	1.530
35.2	3.243	1.942 ± 0.462	1.198	1.818 ± 0.120	1.434
40.0	3.193	4.063 ± 0.742	1.125	2.100 ± 0.193	1.422

[a] Conditions as in Table II.

Cr(hedtaH)(acac) and Cr(hedta)(acac)$^-$ are important solution species is given in eq 8–11. The intermediates CrL-

$$\mathrm{Cr(LH)(acac)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{1}}{\mathrm{Cr(LH)(acac)^*}} \quad (8)$$

$$\mathrm{CrL(acac)^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathbf{2}}{\mathrm{CrL(acac)^{-*}}} \quad (9)$$

$$\mathbf{1} + \mathrm{H_3O^+} \xrightarrow{k_3} \mathrm{CrL(H_2O)} + \mathrm{Hacac} + \mathrm{H_3O^+} \quad (10)$$

$$\mathbf{2} + \mathrm{H_3O^+} \xrightarrow{k_4} \mathrm{CrL(H_2O)} + \mathrm{Hacac} \quad (11)$$

(acac)$^{-*}$ and Cr(LH)(acac)* are suggestive of distorted structures for these species in which bond rupture between Cr(III) and acac$^-$ is at least partially achieved. A similar kinetic route which is less efficient for formation of Cr(edda)$(H_2O)_2^+$ will be discussed in the section on Cr(edda)(acac).

The rate expression for eq 8–11 may be shown to be eq 12 where $[\mathrm{CrL(acac)}]_{tot} = [\mathrm{Cr(hedta)(acac)^-}] + [\mathrm{Cr(hedtaH)(acac)}]$; K_a is the constant from eq 2 for pendant carboxylate protonation. The expression found for k_{obsd} in eq

$$\frac{d[\mathrm{Cr(hedta)(H_2O)}]}{dt} = \frac{[\mathrm{CrL(acac)}]_{tot}}{K_a + [\mathrm{H_3O^+}]}\left\{\frac{k_1k_3[\mathrm{H_3O^+}]^2}{k_{-1} + k_3[\mathrm{H_3O^+}]} + \frac{k_2k_4K_a[\mathrm{H_3O^+}]}{k_{-2} + k_4[\mathrm{H_3O^+}]}\right\} \quad (12)$$

12 reduces to eq 13, the form of eq 7, if the proton scavenging

$$\frac{d[\mathrm{Cr(hedta)(H_2O)}]}{dt} = \frac{k_1}{2} + \frac{k_2K_a}{2[\mathrm{H_3O^+}]}[\mathrm{CrLacac}]_{tot} \quad (13)$$

steps, k_3 and k_4, are each more rapid than reversion of the respective strained intermediates **1** and **2** to the ground-state complexes (i.e., $k_{-1} << k_3[\mathrm{H_3O^+}]$ and $k_{-2} << k_4[\mathrm{H_3O^+}]$; $K_a \simeq [\mathrm{H_3O^+}]$ in these experiments). Under these limiting conditions $A = k_1/2$ and $B = k_2K_a/2$.

Absence of General Acid Catalysis. The effect of free $\mathrm{hedtaH}_n^{(3-n)-}$ as a source of potential general acid catalysis in the aquation reaction of Cr(hedta)(acac)$^-$ was studied at pH 1.40 (λ 350 nm). The ratio of $[\mathrm{Cr(III)}]:[\mathrm{Hacac}]_i$ was 1:7 to ensure full initial formation of the starting complex. Various ratios of $[\mathrm{hedta}]_{tot}:[\mathrm{Cr(hedta)(acac)^-}]_i$ were studied over the range of 0.00 to 15.0:1.00. The rate of dissociation was independent of the amount of uncoordinated $\mathrm{hedtaH}_n^{(3-n)-}$ in the solution. No general acid catalytic path is induced by free hedta ligand, uncoordinated to the Cr(III) center. At pH 1.40 the dominant free ligand hedta species are $\mathrm{hedtaH_2^-}$ and $\mathrm{hedtaH_3}$. The charge repulsion factor between $\mathrm{hedtaH_2^-}$ and Cr(hedta)(acac)$^-$ is not likely to be large. Since at least two protons of $\mathrm{hedtaH_2^-}$ and $\mathrm{hedtaH_3}$ have pK_a's of reasonably high acidity relative to Hacac, it is somewhat surprising that proton transfer to Hacac as a leaving group is not efficient for buffer ions such as $\mathrm{hedtaH_2^-}$ in the solution.

The Cr(edda)(acac) System. The solid complex of Cr(edda)(acac) was isolated. Studies of the acid-catalyzed aquation of Cr(edda)(acac) were not complicated by competitive re-formation since $[\mathrm{Hacac}]/[\mathrm{Cr(III)}]_{tot} = 1.0$. Kinetic data were more scattered as a result of the slower side reaction for acid aquation of edda from the Cr(edda)$(H_2O)_2^+$ product. The acid aquation of Cr(edda)(acac) is not complicated by parallel paths of a protonated form as is the case for Cr(hedta)(acac)$^-$ (eq 8 and 9). However, the dissociative type of intermediate is sufficient to describe the rate dependence

Table IV. Dependence on $[\mathrm{H_3O^+}]$ for the Aquation of Cr(edda)(acac) at 25.0 °C, $\mu = 1.00$

$1/[\mathrm{H_3O^+}]$	$10^{-4} \times k_{obsd}^{-1}$, s	$1/[\mathrm{H_3O^+}]$	$10^{-4} \times k_{obsd}^{-1}$, s
2.00	4.50	5.00	6.69
2.50	4.51	6.00	8.35
4.00	4.74	8.00	8.65
4.55	6.84	10.0	8.75

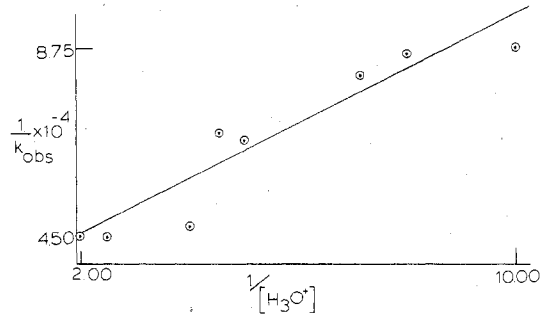


Figure 3. Dependence of the pseudo-first-order rate constant for the acid aquation of Cr(edda)(acac) at 25.0 °C, $\mu = 1.00$; conditions are as in Table IV; see ref 19 concerning the scaling factors of X and Y display.

for the data at 25.0 °C. the data in Table IV conform to the rate expression of eq 14. The agreement to eq 14 is shown

$$\frac{1}{k_{obsd}} = C\frac{1}{[\mathrm{H_3O^+}]} + D \quad (14)$$

in Figure 3.[19] At 25.0 °C, $\mu = 1.00$, $C = (6.26 \pm 1.17) \times 10^3$ M s and $D = (3.34 \pm 0.59)$ 10^4 s as defined by the computer least-squares analysis of Figure 3. Although the apparent form of eq 14 differs from eq 7, both are suggestive of dissociative Cr(III)–acac bond rupture processes. The Cr(edda)(acac) case is given in eq 15–18. The rate expression derived from eq 15–18 is found to be that of eq 17. The apparent first-order rate constant k_{obsd} under pseudo-first-order conditions in $[\mathrm{H_3O^+}]$ may be rearranged into eq 18. From eq 14 and 18 it can be seen that $D = 1/k_5$ and $C = k_{-5}/k_5k_6$.

$$\mathrm{Cr(edda)(acac)} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \underset{\mathbf{3}}{\mathrm{Cr(edda)(acac)^*}} \quad (15)$$

$$\mathbf{3} + \mathrm{H_3O^+} \xrightarrow{k_6} \mathrm{Cr(edda)(H_2O)_2^+} + \mathrm{Hacac} \quad (16)$$

$$\frac{d[\mathrm{Cr(edda)(H_2O)_2^+}]}{dt} = \frac{k_5k_6[\mathrm{H_3O^+}][\mathrm{Cr(edda)(acac)}]}{k_{-5} + k_6[\mathrm{H_3O^+}]} \quad (17)$$

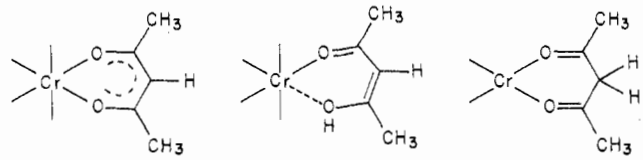
$$\frac{1}{k_{obsd}} = \frac{k_{-5}}{k_5k_6}\frac{1}{[\mathrm{H_3O^+}]} + \frac{1}{k_5} \quad (18)$$

It follows that $k_5 = 2.99 \times 10^{-5}$ s^{-1} and $k_{-5}/k_6 = 0.19$. It is of importance to note that for the Cr(edda)(acac) aquation the reverse step, k_{-5}, is competitive with $k_6[\mathrm{H_3O^+}]$ in contrast to the noncompetitive situation for Cr(hedta)(acac)$^-$. Cr(edda)(acac) cannot have intramolecular associative assistance by means of attack of a pendant alcohol or carboxylic acid functionality which is available for the Cr(hedta)(acac)$^-$ complex. In this regard Cr(edda)(acac) is similar to $\mathrm{Cr(acac)_3}$ which has been studied in its acid-promoted aquation[13] and the substitution of $\mathrm{edtaH^{3-}}$.[12] Banerjea reports the acid-catalyzed aquation of $\mathrm{Cr(acac)_3}$ to proceed with activation parameters[13] $\Delta H^\ddagger = 20.2$ kcal/mol and $\Delta S^\ddagger = -14.2$ eu. Banerjea's interpretation of the mechanism of reaction 19 is

$$Cr(acac)_3 + H_3O^+ \rightarrow Cr(acac)_2(H_2O)_2^+ + Hacac \quad (19)$$

that preequilibrium association of $Cr(acac)_3$ and H^+ (K) is followed by rate-limiting dissociation (k). This interpretation accounts for the observed kinetic data with $k_{Cr(acac)_3/H^+} = Kk$. The $Cr(acac)_3$ acid aquation data are equally well described by eq 15–18 as given for Cr(edda)(acac) if the recombination step $k_{-5} >> k_6[H_3O^+]$, the acid scavenging step to liberate Hacac. Under the assumption, Banerjea's activation parameters may be associated with the ratio k_5k_6/k_{-5} for the analogous steps of eq 15–18 related to $Cr(acac)_3$. Assuming that the ratio k_6/k_{-5} remains relatively constant over the 60–90 °C range studied by Banerjea, then the $\Delta H^\ddagger = 20.2$ kcal/mol may be used for comparison with A and B paths of Cr(hedta)(acac)$^-$. A and B paths both involve proton scavenging of a strained intermediate; the unusual rate dependence is a consequence of the pendant group protonation (eq 2). Reasonably comparable activation enthalpies for A, B, and $Cr(acac)_3/H_3O^+$ paths are noted: 21.3 kcal/mol; 16.7 kcal/mol; 20.2 kcal/mol, respectively. Hence the total cost of bond adjustments is similar in all three paths for Cr–O bond rupture. The comparable data for activation entropies cannot be rigorously applied. All inaccuracies in the assumption that (k_6/k_{-5}) remains constant contributes to a determinant error in $\Delta S^\ddagger$ for the k_5 step. However, Banerjea's data for the uncatalyzed dissociation of acac$^-$ gives $\Delta H^\ddagger = 13.8$ kcal/mol and $\Delta S^\ddagger = -37.3$ eu.[13] The more negative value by 17 eu is consistent with the charge-separating process for the uncatalyzed path. The charge separation should cost more in entropy. Assuming that the proton-promoted path for loss of one Hacac from $Cr(acac)_3$ is no more certain than 5 eu, due to the assumption concerning k_6/k_{-5}, allows assignment of $\Delta S^\ddagger = -14.2 \pm 5$ eu for comparison to the corresponding parameters with Cr(hedta)(acac)$^-$. The B path is a composite kinetic term, $k_2K_a/2$. If the assumption is made that K_a exhibits a similar temperature dependence as acetic acid, the parameters may be corrected by addition of the $\Delta H°$ and $\Delta S°$ for $K_a/2$ to the experimental values. For the temperature range used in the Cr(hedta)(acac)$^-$ study the K_a values of acetic acid are readily available.[14] A linear least-squares analysis of $-\ln K_a$ vs. $1/T$ for acetic acid yields $\Delta H° = -0.69$ kcal/mol and $\Delta S° = -22.7$ eu. These values allow an estimated set of parameters for the intrinsic k_2 step of the B path to be calculated: $\Delta H^\ddagger = 17.4$ kcal/mol, $\Delta S^\ddagger = +1.3$ eu. If this estimate on the effect of K_a is correct, both the k_1 and k_2 paths are found to have similar values of $\Delta S^\ddagger$ ($\simeq 0 \pm 2$ eu) for the Cr(hedta)(acac)$^-$ system. These values for $\Delta S^\ddagger$ may then be compared to the $\Delta S^\ddagger = -14.2 \pm 5$ eu for the dissociation of Hacac from $Cr(acac)_3$ in which Cr–O bond rupture must proceed without intramolecular assistance. Systems which lack intramolecular assistance for aquation of Hacac, Cr(edda)(acac), and $Cr(acac)_3$ exhibit the characteristically slow ligand exchange reactions of Cr(III) centers ($k_{obsd} \sim 10^{-5}$ s^{-1}) and the negative activation entropies due to the costs of adjusting the Cr–O bonds without compensation.[15] When pendant groups are available to attack the face of the CrL_6 octahedron, compensation from bond making to a new oxygen donor can occur for the straining of the Cr–O bonds of the Cr–acac component. Trading one O donor in octahedral coordination for two more weakly coordinated O donors in seven-coordination apparently lowers the entropy barrier from −14 eu to nearly 0 eu. The advantage of the carboxylate pendant functionality in Cr(hedta)(acac)$^-$ or Cr(hedtaH)(acac) species when oriented in the facial position is that it is then correctly poised to scavenge the second O-donor position of the leaving Hacac with only minor additional adjustments of the glycinato in-plane ring.

It is kinetically impossible to know whether the scavenging proton step involves association at an oxygen or at the central carbon of the leaving Hacac (structures II and III). Re-



I II III

arrangement of the enol to keto forms of the free Hacac would be proton transfer limited and therefore much faster than any of the rate-limiting distortions about Cr(III). Banerjea has interpreted his data for the proton dissociation of Hacac from $Cr(acac)_3$ as proceeding with a monodentate acac$^-$ intermediate. The data are consistent with this view, but it is not uniquely restricted to this path nor is it any less consistent with Cr–O bond distortion without complete bond rupture in the transition state. There is evidence that the loss for Hacac is a virtually concerted removal of both O-donor groups from the Cr(III) center in $Cr(acac)_3$. ^{18}O exchange studies show that no ^{18}O is incorporated into the acac$^-$ oxygens of chelated $Cr(acac)_3$.[16] If a monodentate form of acac$^-$ remained coordinated, exchange of the terminal O is anticipated to be rapid based on the rapidity of the free ligand ^{18}O-exchange process.[16] The structure shown by II is sensible in that the O–H bond formation further weakens the Cr–O bond. However, a structure III analogue has been observed by the stopped-flow Fourier transfer ^1H NMR method for a diamagnetic Co^{III}–acacH intermediate in the acid aquation of $Co(acac)_3$.[17] The rehybridized structure III would also facilitate a rapid, simultaneous loss of both O donors from Cr(III). This is due to the much poorer basicity of the keto oxygens relative to the pseudoaromatic and anionic oxygens of the ground-state Cr–acac bonds. Some support for structure III as the active species in the acid dissociation pathways for Hacac from Cr(III) centers is implied by the reversible reaction at high [Hacac] ($[Hacac]/[Cr(III)]_{tot} > 25$) in the pH range of 1.2–1.8. The keto form is the most abundant form of 2,4-pentanedione. In order for collisions of Cr(hedta)(H_2O) species to be efficient in re-formation of Cr(hedta)(acac)$^-$, it would seem more probable if the species protonated at carbon were the kinetically active species. However, rapid conversion to the enol form on association of one of the Hacac O donors cannot be excluded unambiguously as a possible re-formation path.

Evaluation of the Formation Constant of Cr(hedta)(acac)$^-$. Samples of 0.40 M Hacac and 2.84×10^{-3} M total Cr(hedta) were brought to equilibrium at pH 7.50 ($\mu = 0.20$, T = 25.0 °C). Under this condition the Cr(hedta)(acac)$^-$ is fully formed. The samples were acidified to various values of $[H_3O^+]$ between 1.0×10^{-4} and 10.0×10^{-4} M and allowed to reach equilibrium at 25.0 °C for 2 days. The 2-day spectra were constant after an additional 9 days. Absorption spectra and data at fixed wavelengths were recorded and the equilibrium value of H_3O^+ was measured for each sample at 25.0 °C, $\mu = 0.20$. The mass balance expression for total Cr(III) and Beer's law may be combined with eq 1 into the expression of eq 20 where A is the observed absorbance (corrected for the blank), b is the path length (1.00 cm in this experiment), and $[Cr(III)]_{tot}$ is the sum of all Cr(III) species. The best data were obtainable at 350 nm where $\epsilon_{Cr(hedta)acac^-}$ had a value of 938 M^{-1} cm^{-1} and $\epsilon_{Cr(hedta)(H_2O)}$ had a value of 341 M^{-1} cm^{-1}. The linear agreement of the data to eq 20 was confirmed at 350 and 543 nm. Both plots had a zero intercept within experimental error and a linear dependence in $[H_3O^+]$ (see Figure 4).[19] From the slope of the data at 350 nm, K_1 was

$$\{((A/b[Cr(III)]_{tot}) - \epsilon_{Cr(hedta)(acac)^-})[Hacac]\}/$$
$$(\epsilon_{Cr(hedta)(H_2O)} - (A/b[Cr(III)]_{tot})) = (1/K_1)[H_3O^+] \quad (20)$$

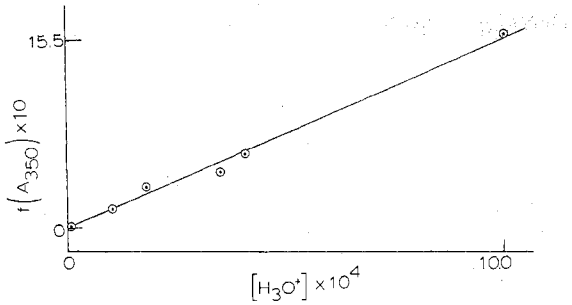


Figure 4. Determination of K_1 by competition of Cr(hedta)(H_2O) and H_3O^+ for $acac^-$ at 25.0 °C, μ = 0.20; see ref 19 concerning X and Y scaling; $[Cr(III)]_{tot}$ = 2.841 × 10^{-3} M, [Hacac] = 0.40 M; f(A_{350}) is given by the left-hand side of eq 20.

found to be (6.69 ± 0.27) × 10^{-4}. When combined with the value of K_a' for Hacac, K_f is found to be (5.87 ± 0.24) × 10^5 M^{-1} for the association of Cr(hedta)(H_2O) and $acac^-$.[18] The comparison between K_f for $acac^-$ and values of monodentate anion donors (K_x) can now be made. Normal values of K_x are ≤20 M^{-1}.[9,10] The relative ratio of $K_f/K_x \simeq 2.9 \times 10^4$. This would seem to be a reasonable result since the formation constant of a chelate ring vs. two equivalent monodentate donors is usually ca. 10^3–10^4 (e.g., ethylenediamine vs. 2 NH_3, etc.). Since the magnitude of the ratio of K_f/K_x is not abnormally large, one can also conclude that the interaction of the nonbonding π t_{2g}^3 electrons of Cr(III) with empty π^* levels of the $acac^-$ anion contributes relatively little to the bonding of $acac^-$ to the Cr(III) center of Cr(hedta); this conclusion is further collaborated by the absence of any new MLCT band in the visible spectrum.

Summary

It appears certain that the pendant carboxylate functionality of Cr(hedta)(acac)$^-$ is responsible for the enhanced lability of the Cr(III) center and the accelerated rate of aquation of Hacac relative to Cr(edda)(acac) and $Cr(acac)_3$. The stability of the Cr(hedta)(acac)$^-$ complex is enhanced by the normal chelate effect relative to simple monodentate anion donors. The effect of the alcohol functionality as an intramolecular labilizing group is currently being assessed on a related set of ligands. However, the low energy barrier for substitution of Hacac on Cr(hedta)(H_2O) or removal of Hacac from Cr(hedta)(acac)$^-$ would appear to be lowest for the carboxylate group in recognition of the fact that chelate ring formation of a glycinato fragment, concerted with the loss of Hacac, would require fewer sequential steps for the aquation process. Indeed, the protonated carboxylate A path is intrinsically less efficient than the unprotonated B path (protonation refers to the pendant group and not the required protonation for the leaving $acac^-$). Using the estimated value of K_a (eq 2) the parameters at 26.0 °C show that $(k_2/k_1) \simeq 51$. Therefore, the approach of the anionic carboxylate group is favored to assist displacement of $acac^-$ relative to its protonated form.

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Registry No. Cr(hedta)(acac)$^-$, 68070-88-2; Cr(edda)(acac), 26085-42-7.

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(18) The small absorbance changes and ratio of difference terms in eq 20 yield larger error in K_f as determined at 350, 387, and 546 nm. K_f is not considered to be more accurate than ±50% although the precision at a given wavelength is within ±5%.
(19) The least-squares graphics subroutines for the DECLAB 11/03 computer are written with scaling factors for the X and Y axes such that the maximum expansion of the graphics terminal display is obtained in the hard copy output. The numerical data are obtained for the slope and intercept with appropriate standard deviations in a separate statement together with an input data listing.