

and-ligand contacts. The lower yield and the longer reaction times found in the formation of **3** and **4** starting from the diiodide **1** are probably due to the lower halide scavenging capacity of the ammonium ions with respect to the silver ion. In all the reactions described above the behavior of the nitrosyl ligand is noteworthy. The net result of forcing the rhodium and iridium complexes to have trigonal-bipyramidal geometry with an axial nitrosyl group is a reduction of the central metal **2** (d^6) \rightarrow **3**, **4** (d^8) due to interconversion of nitrosyl bonding mode. The further reduction to d^{10} configuration in the triphenylphosphine case can be due as pointed out above to the reducing power of the phosphine itself.

In these reactions the nitrosyl ligand is acting as an electron sink, as suggested by Collman et al.^{4,6} Those observations further support the hypothesis that the higher reactivity of the nitrosyl complexes in comparison to the carbonyl analogues is probably due to the ambivalent character of the nitrosyl ligand.

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Registry No. **1a**, 25544-86-9; **1b**, 40241-25-6; **2a**, 59983-15-2; **2b**, 60018-66-8; **3a**, 59983-17-4; **3b**, 59983-19-6; **4a**, 59983-21-0; **4b**, 59983-23-2; **5**, 42712-02-7; **6**, 25448-15-1; **7**, 59983-24-3; **8**, 59982-92-2.

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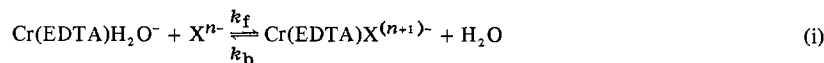
Rapid Equilibration of the Ethylenediamine-*N,N,N',N'*-tetraacetatoaquochromate(III) Complex with Chromate(VI), Molybdate(VI), Tungstate(VI), and Azide. Labilization of the Aquo Ligand by the Free Carboxylate and Substitution at Chromium(III)

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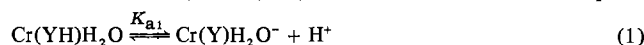
Equilibration kinetic studies on the rapid complexation of ethylenediamine-*N,N,N',N'*-tetraacetatoaquochromate(III), $\text{Cr}(\text{EDTA})\text{H}_2\text{O}^-$, with chromate(VI), molybdate(VI), and tungstate(VI) have been carried out using the stopped-flow method at 25 °C, pH in the range 7.3–8.7, and $I = 1.0 \text{ M}$ (LiClO_4). Replacement of the coordinated H_2O



which is labilized by the free carboxylate arm of the EDTA is observed. Temperature-jump and stopped-flow studies of (i) with $\text{X}^{n-} = \text{azide}$ have also been carried out at pH 4.3–5.4 and pH 7.38, respectively. The hydrogen ion dependence of k_f is in all cases given by $k_1 + k_2[\text{H}^+]$, where k_2 makes $\leq 25\%$ contributions with molybdate(VI) and azide and $\leq 10\%$ with chromate(VI) and tungstate(VI). Rate constants k_1 ($\text{M}^{-1} \text{s}^{-1}$) are 3.2 ± 0.2 (CrO_4^{2-}), 21 ± 2 (MoO_4^{2-}), 27 ± 4 (WO_4^{2-}), and 98 ± 5 (N_3^-). Kinetic equilibrium constants $K_1 = k_f/k_b$ are in good agreement with those obtained spectrophotometrically.

It has been shown previously that the $\text{Cr}(\text{III})$ -EDTA complex is quinquedentate and contains a coordinated H_2O .¹ Unlike the case of the $\text{Co}(\text{III})$ analogue there is no evidence for a sexadentate EDTA complex.² Thus samples of $\text{Cr}(\text{EDTA})\text{H}_2\text{O}^-$ retain the coordinated H_2O when left in a desiccator in vacuo over P_2O_5 for 7 days or when kept at ca. 100 °C for 1 day.³ Evidence for the free carboxylate group has been obtained from ir spectroscopy.⁴ The complex can

also be titrated with base to yield two acid dissociation constants; see (1) and (2) ($\text{EDTA} = \text{Y}^{4-}$). At 18 °C, $\text{p}K_{a1}$



$= 2.27$, and $\text{p}K_{a2} = 7.41$, $I = 0.15 \text{ M}$.⁵ Whereas chromium(III) is normally inert to substitution and there is a vast

literature to support this,⁶ in the present work rapid complexation at the chromium(III) is observed and fast reaction techniques are required.

Experimental Section

Materials. AnalaR grade sodium perchlorate, sodium dichromate, sodium molybdate, sodium tungstate, and sodium hydroxide were used. Triethanolamine (TEA) was reagent grade and not purified further. Lithium perchlorate was prepared from 72% perchloric acid (AnalaR) and lithium carbonate (GPR) and was recrystallized until free of impurities. The complex Cr(YH)H₂O was prepared by the method of Hamm.⁷ Stock solutions of chromate (1.0 M) were made by the addition of sodium hydroxide to sodium dichromate and adjusting the pH to 7.5. Stock solutions of sodium tungstate required the addition of small amounts of 5 M perchloric acid to bring the pH into the range 7.5–8.0.

Adjustment of pH. All measurements were made in the presence of TEA buffer ≥ 0.05 M, at 25 °C, $I = 1.0$ M (LiClO₄). With azide the ionic strength was adjusted with NaClO₄. When LiClO₄ was used, solutions contained as much as 0.2 M Na⁺; in the reaction with molybdate at least this does not affect the measured pH values. Measurement of pH was carried out on a Radiometer PHM4 meter with G202C glass and K401 calomel electrodes, the latter containing saturated NaCl. The meter was calibrated at $I = 1.0$ M (NaClO₄ or LiClO₄) using solutions of known [H⁺] in the range 0.001–0.100 M. The protonation constant of 2.16×10^5 M⁻¹ at 25 °C for azide N₃⁻ was determined by potentiometric titration.

Formation Constants. Equilibrium formation constants were determined using a Unicam SP500 spectrophotometer by analyzing the dependence of absorbance on pH and [Xⁿ⁻]_T. The latter represents the total added concentration of Xⁿ⁻, which is in large (>10-fold) excess of [Cr(III)]_T. The value of pK_{a2} was also determined at $I = 1.0$ M by spectrophotometric titration.

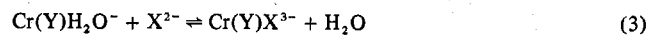
Kinetic Measurements. Kinetic studies, pH 7.3–8.5, were carried out using a Durrum-Gibson stopped-flow spectrophotometer with the wavelength in the 500–600-nm range. Rate constants were determined with [Xⁿ⁻] in >10-fold excess; values quoted are the average of a number of determinations (usually three). The effects of deaeration of solutions with N₂ to remove dissolved CO₂ and of varying [TEA] and [Cr(III)]_T were investigated, as well as the variation in pH and [Xⁿ⁻]_T. Type SBA7 temperature-jump equipment (Messanlagen, Göttingen) was used for the azide study, pH 4.3–5.4, λ 440 nm.

Treatment of Data. Kinetic and equilibrium data were analyzed with the aid of a nonlinear least-squares program⁸ with weighting y^{-2} , where y is the dependent variable, e.g., k_{obsd} . This approach is consistent with constant-percentage errors on y .

Results

Acid Dissociation Constant for Cr(Y)H₂O. The constant pK_{a2} as defined in (2) was determined at 25 °C by pH titration and found to be 7.25, $I = 1.0$ M (LiClO₄), and 7.20, $I = 1.0$ M (NaClO₄), in satisfactory agreement with literature values.⁹

Formation Constants. The addition of chromate(VI), molybdate(VI), and tungstate(VI) to Cr(Y)H₂O⁻/Cr(Y)OH²⁻ at pH >7 gave visible spectrophotometric changes. Details of peak positions (λ , nm; ϵ , M⁻¹ cm⁻¹) for Cr(Y)(MoO₄)³⁻ (λ 405, ϵ 106; λ 571, ϵ 176) and Cr(Y)(WO₄)³⁻ (λ 410, ϵ 111; λ 565, ϵ 181) were obtained. It was difficult to obtain similar details for the chromate complex because at the concentrations required to give extensive complex formation Cr(VI) also gave a strong absorption. Formation constants, K_1 , as defined in (3) were determined at λ 570 nm for Mo(VI) and W(VI).



Molar absorption coefficients at any particular [H⁺] and [X²⁻]_T, ϵ_{obsd} , are given by (4) where ϵ_{OH} , ϵ_{A} (both known,

$$\epsilon_{\text{obsd}} = \frac{\epsilon_{\text{OH}}K_{\text{a2}} + \epsilon_{\text{A}}[\text{H}^+] + \epsilon_{\text{C}}K_1[\text{H}^+][\text{X}^{2-}]_{\text{T}}}{K_{\text{a2}} + [\text{H}^+] + K_1[\text{H}^+][\text{X}^{2-}]_{\text{T}}} \quad (4)$$

Table I), and ϵ_{C} are the absorption coefficients for Cr(Y)OH²⁻, Cr(Y)H₂O⁻, and Cr(Y)X³⁻, respectively. This dependence of ϵ_{obsd} on pH is illustrated for W(VI) in Figure 1. Values of K_1 (Table VI below) and ϵ_{C} (Table I) obtained by a

Table I. Absorption Coefficients (M⁻¹ cm⁻¹) As Determined Experimentally (ϵ_{OH} and ϵ_{A}) and As Evaluated from Equilibrium Constant Determination (ϵ_{C})

	λ 550 nm	λ 570 nm
ϵ_{OH}	105 ^a	121 ^a
ϵ_{A}	200 ^a	174 ^a
$\epsilon_{\text{C}}(\text{Cr})$	190 ^b	
$\epsilon_{\text{C}}(\text{Mo})$		176 ^c
$\epsilon_{\text{C}}(\text{W})$		179 ^c

^a Determined by direct measurement at appropriate pH.
^b From fit to eq 5. ^c From fit to eq 4.

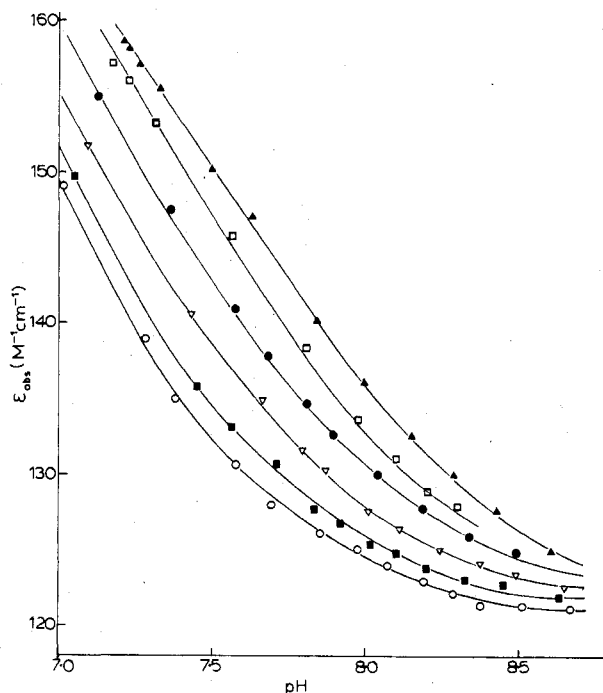


Figure 1. Dependence of ϵ_{obsd} on [WO₄²⁻] and pH for the reaction of Cr(EDTA)OH₂⁻ with W(VI) at 25 °C, $I = 1.0$ M (LiClO₄), [WO₄²⁻] = 0.00 M (○), 0.01 M (■), 0.025 M (▽), 0.05 M (●), 0.075 M (□), and 0.10 M (△), and λ 570 nm.

least-squares fit of ϵ_{obsd} to (4) are as listed.

In order to determine K_1 for Cr(VI) the concentration of the latter was varied at two fixed pH values, 7.51 and 8.11, λ 550 nm. Equation 4 can be rearranged to give (5) where

$$(\epsilon_{\text{obsd}} - \epsilon_{\text{app}})^{-1} = (\epsilon_{\text{C}} - \epsilon_{\text{app}})^{-1} (1 + [\text{H}^+]/K_{\text{app}}[\text{X}^{2-}]) \quad (5)$$

$\epsilon_{\text{app}} = \epsilon_{\text{OH}}K_{\text{a2}} + \epsilon_{\text{A}}[\text{H}^+]/(K_{\text{a2}} + [\text{H}^+])$ and $K_{\text{app}} = K_1/(K_{\text{a2}} + [\text{H}^+])$. Values of $K_1 = 79 \pm 15$ (pH 7.51) and 77 ± 4 (pH 8.11) evaluated from Figure 2 are in satisfactory agreement. The average of these is given in Table VII. The value of ϵ_{C} obtained is given in Table I.

The equilibrium constant for formation of the azide complex has been determined previously.¹⁰

Kinetics. With the Cr(VI), Mo(VI), or W(VI) reactant in large excess, plots of $\log(A - A_t)$ against time were linear to at least 2 half-lives. From the slopes ($\times 2.303$) first-order equilibration rate constants, k_{eq} , were obtained. In preliminary experiments, Table II, k_{eq} was found to be independent ($\pm 6\%$) of buffer [TEA] and of [Cr(III)]_T, as well as presence or absence of atmospheric CO₂. At constant [H⁺] a linear dependence of k_{eq} on [X²⁻]_T was observed in all three studies, Figures 3 and 4, consistent with equilibration kinetics. Assuming Cr(Y)H₂O⁻ and not Cr(Y)OH²⁻ is a reactant the expression

$$k_{\text{eq}} = \frac{k_f[\text{H}^+][\text{X}^{2-}]_{\text{T}}}{[\text{H}^+] + K_{\text{a2}}} + k_b \quad (6)$$

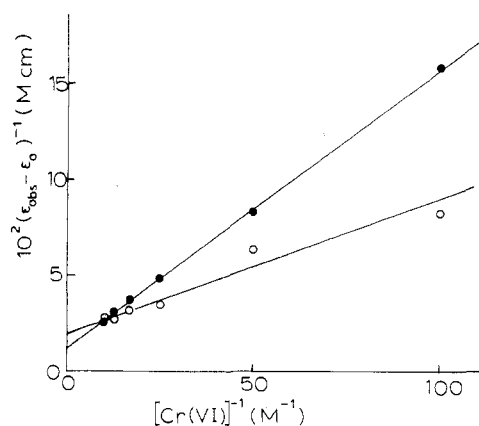


Figure 2. Benesi-Hildebrand plots, eq 5, for the determination of K_1 for the reaction of $\text{Cr}(\text{EDTA})\text{OH}_2^-$ with $\text{Cr}(\text{VI})$ at 25°C , $I = 1.0\text{ M}$ (LiClO_4), pH 7.51 (\circ) and 8.11 (\bullet), and λ 550 nm.

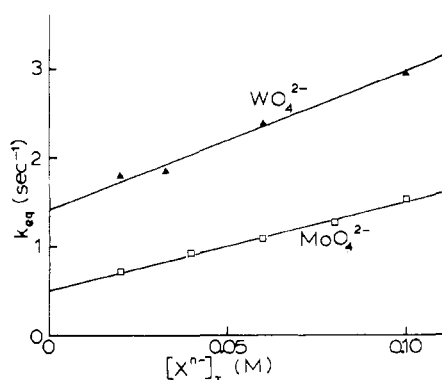


Figure 3. First-order dependence of k_{eq} on $[\text{X}^{n-}]_{\text{T}}$ at 25°C , pH 7.51, $[\text{TEA}] = 0.1\text{ M}$, and $I = 1.0\text{ M}$ (LiClO_4), for the reactions of $\text{Cr}(\text{EDTA})\text{OH}_2^-$ with $\text{Mo}(\text{VI})$ (\square) and $\text{W}(\text{VI})$ (\blacktriangle).

Table II. Preliminary Experiments (25°C) on the Reactions of $\text{Cr}(\text{EDTA})\text{H}_2\text{O}^-$ with $\text{Cr}(\text{VI})$, $\text{Mo}(\text{VI})$, and $\text{W}(\text{VI})$ at pH 7.81, $I = 1.00\text{ M}$ (LiClO_4), with $[\text{Cr}(\text{VI})]$ and $[\text{Mo}(\text{VI})] = 0.10\text{ M}$ and $[\text{W}(\text{VI})] = 0.075\text{ M}^a$

$10^3[\text{Cr}(\text{III})]_{\text{T}},^b$ M	$[\text{TEA}],^c$ M	CO_2^d	$k_{\text{eq}}, \text{s}^{-1}$		
			Cr(VI)	Mo(VI)	W(VI)
0.42	0.10	Absent	0.133	1.03	2.01
0.42	0.20	Absent	0.129	0.98	1.90
1.97	0.20	Absent	0.130	0.92	1.88
0.50	0.10	Present	0.138	0.98	1.98
0.50	0.05	Present		0.94	1.91

^a No significant dependence is observed on $[\text{TEA}]$, $[\text{Cr}(\text{III})]_{\text{T}}$, and whether or not CO_2 is present. ^b EDTA complex. ^c Buffer. ^d Atmospheric CO_2 was removed by bubbling N_2 .

applies, where k_f and k_b are the forward and back rate constants for (3). Equation 6 can be rewritten as (7). On

$$k_{\text{eq}} = k_f \left(\frac{[\text{H}^+][\text{X}^{n-}]_{\text{T}}}{[\text{H}^+] + K_{a2}} + \frac{1}{K_1} \right) \quad (7)$$

varying $[\text{H}^+]$ over the pH range 7.3–8.7 the $[\text{H}^+]$ dependence (8) was observed for k_f . Rate constants k_{eq} are listed for $k_f = k_1 + k_2[\text{H}^+]$ (8)

$\text{Cr}(\text{VI})$ (Table III), $\text{Mo}(\text{VI})$ (Table IV), and $\text{W}(\text{VI})$ (Table V). The k_2 term contributes $\leq 25\%$ to k_f in the case of $\text{Mo}(\text{VI})$ but is less well defined ($\leq 10\%$ contributions) for $\text{Cr}(\text{VI})$ and $\text{W}(\text{VI})$.

The azide reaction was fast enough to study by the temperature-jump technique at pH's in the range 4.3–5.4 and was

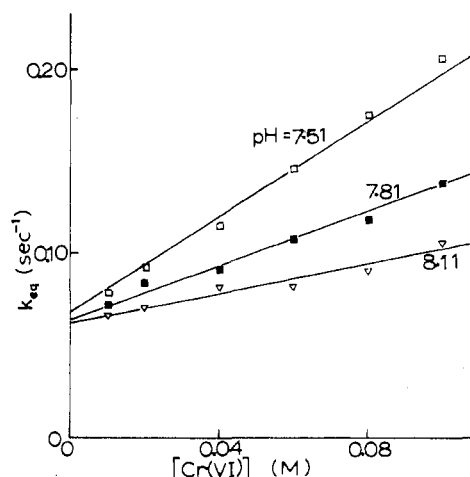


Figure 4. Dependence of k_{eq} on $[\text{CrO}_4^{2-}]$ for the reaction of $\text{Cr}(\text{EDTA})\text{OH}_2^-$ with $\text{Cr}(\text{VI})$ at 25°C , $I = 1.0\text{ M}$ (LiClO_4), and pH 8.11 (∇), 7.81 (\blacksquare), and 7.51 (\square).

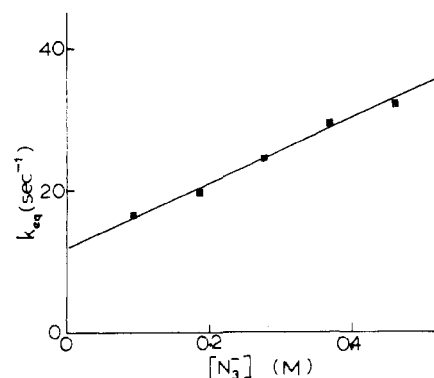


Figure 5. Dependence of k_{eq} on $[\text{N}_3^-]$ for the reaction of $\text{Cr}(\text{EDTA})\text{OH}_2^-$ with azide at 25°C , $I = 1.0\text{ M}$ (LiClO_4), and pH 7.38.

Table III. Pseudo-First-Order Rate Constants, k_{eq} , for the Equilibration of the Cr^{III} -EDTA Complex with $\text{Cr}(\text{VI})$ at 25°C , $I = 1.00\text{ M}$ (LiClO_4), $[\text{Cr}(\text{III})]_{\text{T}} = 0.5 \times 10^{-3}\text{ M}$, and $[\text{TEA}] = 0.10\text{ M}$

$[\text{Cr}(\text{VI})]_{\text{T}}, \text{M}$	pH	$k_{\text{eq}}, \text{s}^{-1}$	$k_{\text{calcd}},^a \text{s}^{-1}$
0.010	7.51	0.079	0.081
	7.81	0.072	0.071
	8.11	0.067	0.066
0.020	7.51	0.092	0.093
	7.81	0.084	0.079
	8.11	0.070	0.070
0.040	7.51	0.115	0.119
	7.81	0.091	0.093
	8.11	0.082	0.078
0.060	7.51	0.146	0.145
	7.81	0.107	0.108
	8.11	0.082	0.086
0.080	7.51	0.175	0.171
	7.81	0.118	0.123
	8.11	0.090	0.094
0.100	7.51	0.206	0.196
	7.81	0.138	0.137
	8.11	0.105	0.102

^a From the least-squares computer fit of data to (7) and (8).

investigated under these conditions and by the stopped-flow technique at pH 7.38. The agreement of data was good. For the lower pH range an allowance was made for $[\text{HN}_3]$. Reciprocals of temperature-jump relaxation times τ^{-1} are equivalent to k_{eq} , Table VI, where a good fit to (8) is again observed, Figure 5 (contributions from $k_2 \leq 25\%$). Values of

Table IV. Pseudo-First-Order Rate Constants, k_{eq} , for the Reaction of the Cr^{III}-EDTA Complex with Mo(VI) at 25 °C, $I = 1.00$ M (LiClO₄), with $[\text{Cr(III)}]_{\text{T}} = 1.0 \times 10^{-3}$ M and $[\text{TEA}]_{\text{T}} = 0.05$ M, Except Where Indicated

[Mo(VI)] _T , M	pH	k_{eq} , s ⁻¹	$k_{\text{calcd.}}^a$, s ⁻¹	
0.010	7.33	0.65	0.68	
	7.60	0.64	0.58	
	7.77	0.59	0.54	
	8.05	0.54	0.50	
0.020	7.51 ^b	0.71	0.70	
	0.025	7.31	0.81	0.87
0.025	7.60 ^c	0.61	0.69	
	7.86	0.56	0.59	
	8.11	0.59	0.53	
	8.64	0.54	0.48	
	0.040	7.51 ^b	0.92	0.87
	0.050	7.31	1.21	1.18
		7.60 ^c	0.81	0.88
		7.87	0.70	0.70
		8.12	0.63	0.60
		8.48	0.54	0.52
8.64 ^d		0.53	0.50	
8.64 ^e		0.52	0.50	
8.64		0.49	0.50	
0.060		7.51 ^b	1.08	1.04
0.075		7.86	0.85	0.82
	8.11	0.67	0.67	
	8.35	0.50	0.58	
	8.64	0.46	0.52	
	0.080	7.51 ^b	1.27	1.22
0.100	7.51 ^b	1.53	1.39	
	7.68	1.14	1.13	
	8.05	0.75	0.77	
	8.35	0.58	0.62	
	8.65	0.51	0.53	

^a From the least-squares computer fit to (7) and (8). ^b $[\text{Cr(III)}]_{\text{T}} = 0.5 \times 10^{-3}$ M, $[\text{TEA}] = 0.10$ M. ^c $[\text{TEA}] = 0.10$ M. ^d $[\text{Cr(III)}]_{\text{T}} = 4.0 \times 10^{-3}$ M. ^e $[\text{Cr(III)}]_{\text{T}} = 2.0 \times 10^{-3}$ M.

Table V. Pseudo-First-Order Rate Constants, k_{eq} , for the Reaction of the Cr^{III}-EDTA Complex with W(VI) at 25 °C, $I = 1.00$ M (LiClO₄), with $[\text{Cr(III)}]_{\text{T}} = 1.0 \times 10^{-3}$ M and $[\text{TEA}]_{\text{T}} = 0.05$ M, Except Where Indicated

[W(VI)], M	pH	k_{eq} , s ⁻¹	$k_{\text{calcd.}}^a$, s ⁻¹	
0.010	7.37	1.67	1.76	
	7.63	1.68	1.65	
	7.79	1.57	1.62	
	7.85	1.70	1.60	
	8.05	1.52	1.57	
0.020	7.51 ^b	1.80	1.80	
0.025	7.38	1.87	1.93	
	7.60	1.81	1.79	
	7.75	1.76	1.72	
	7.85	1.80	1.68	
	8.06	1.61	1.62	
	0.033	7.51 ^b	1.85	1.93
	0.050	7.68	2.07	1.95
		7.85	1.89	1.83
7.88		1.85	1.81	
8.17		1.67	1.67	
8.17 ^c		1.70	1.67	
8.65		1.64	1.56	
8.65 ^d		1.50	1.56	
0.060		7.51 ^b	2.40	2.21
0.075		8.15	1.80	1.76
		8.17 ^c	1.80	1.75
	0.100	7.51 ^b	2.95	2.62
0.100	8.16	1.85	1.83	
	8.20 ^c	1.88	1.81	
	8.64 ^d	1.53	1.62	

^a From the least-squares computer fit to (7) and (8). ^b $[\text{Cr(III)}]_{\text{T}} = 0.5 \times 10^{-3}$ M, $[\text{TEA}] = 0.10$ M. ^c $[\text{Cr(III)}]_{\text{T}} = 4.0 \times 10^{-3}$ M. ^d $[\text{Cr(III)}]_{\text{T}} = 2.0 \times 10^{-3}$ M.

k_1 , k_2 , $K_1(\text{kin})$, and $K_1(\text{spec})$ from least-squares fits are given in Table VII along with k_{-1} from k_1 and $K_1(\text{kin})$.

Table VI. Pseudo-First-Order Rate Constants, k_{eq} , for the Reaction of the Cr^{III}-EDTA Complex with Azide at 25 °C, $I = 1.00$ M (NaClO₄), with $[\text{Cr(III)}]_{\text{T}} = (1.1-7.5) \times 10^{-3}$ M

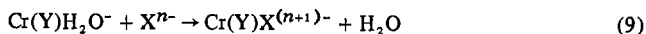
[N ₃ ⁻] _T , M	pH	k_{eq} , s ⁻¹	$k_{\text{calcd.}}^a$, s ⁻¹	
(a) Stopped-Flow Studies				
0.092	7.38	16.6	16.9	
	0.18	7.38	19.8	20.6
	0.28	7.38	24.5	24.1
	0.37	7.38	29.4	27.7
	0.46	7.38	32.4	31.3
	(b) Temperature-Jump Studies			
0.05	5.00	17	17	
0.10	5.05	23	22	
0.20	5.28	33	31	
0.30	5.34	38	40	
0.30	4.34	31	31	
0.40	5.20	46	48	

^a From the least-squares computer fit to (7) and (8), allowance being made for $[\text{HN}_3]$ in temperature-jump studies.

Discussion

The results obtained in this work illustrate the quite remarkable labilizing effect which an uncoordinated carboxylate group attached to an existing ligand has on the substitution properties of a Cr(III) metal complex. The labilizing effect is such that in the present work fast-reaction techniques are required for kinetic studies. Previously it has been demonstrated that for the conversion of the quadridentate Cr^{III}-EDTA-H₂O complex to the quinquadentate form, with a free unprotonated carboxylate of the EDTA replacing a coordinated H₂O, the rate constant is 330 s⁻¹ at 25 °C.¹¹ Ogino et al. have recently demonstrated that there is also a rapid equilibration of quinquadentate Cr^{III}-EDTA with acetate (replacement of coordinated H₂O by CH₃CO₂⁻).¹⁰ The interpretation with azide is straightforward but with Cr(VI), Mo(VI), and W(VI) there exists the possibility of substitution at the Cr(VI), Mo(VI), and W(VI) centers, with retention of the Cr^{III}-O bond. This possibility seems unlikely however from parallel studies with the Cr^{III}-MED3A complex, Cr-(MED3A)H₂O (MED3A = *N*-methylethylenediamine-*N,N,N'*-triacetate), where the methyl group is unable to labilize the coordinated H₂O.¹⁰ Thus with Cr(VI) as reactant (0.04 M) at pH 7.5 a slow equilibration $k_{\text{eq}} \approx 4 \times 10^{-4}$ s⁻¹ is observed, whereas the much higher values of k_{eq} in Table III leave no doubt that with the Cr^{III}-EDTA complex rapid substitution at the Cr(III) is occurring. With Mo(VI) and W(VI) equilibration studies with the Cr^{III}-MED3A complex are also appreciably slower. Thus if substitution occurs at Mo(VI) and W(VI), the most effective pathway is that involving the protonated forms HMoO₄⁻ and HWO₄⁻ (since an oxo ligand is being displaced), and rate constants are respectively 25 and 50 times slower for the reaction of HMoO₄⁻ and HWO₄⁻ with Cr(MED3A)OH²⁻ than for the corresponding reactions with Cr(EDTA)OH²⁻. Since there is a less favorable electrostatic factor in the case of Cr(EDTA)OH²⁻, the most likely conclusion is that substitution is at Cr(III) for the Cr^{III}-EDTA complex. Furthermore a feature of the reactions of Co(NH₃)₅H₂O³⁺ with Mo(VI) and Cr-(MED3A)H₂O with Mo(VI) and W(VI) (when substitution is at Mo(VI) and W(VI)) is the occurrence of terms second order in the VI state ion. These are absent in the present study.

For the range of conditions investigated the k_1 term in (8) is dominant in each case. The reactants are believed to be the aquo complex and unprotonated substituent (which is the major species), Xⁿ⁻, as in (9). Alternatively the k_1 term could



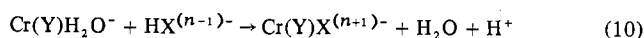
arise from a pathway involving Cr(Y)OH²⁻ + HX⁽ⁿ⁻¹⁾⁻. We consider this unlikely since OH⁻ is generally a poor leaving

Table VII. Kinetic and Equilibrium Data for the Reactions of $\text{Cr}(\text{Y})\text{H}_2\text{O}^-$ with Various Ligands, X^{n-} , at 25 °C, $I = 1.00 \text{ M}$ (LiClO_4)

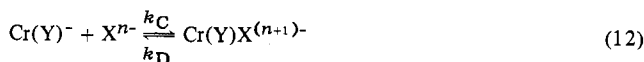
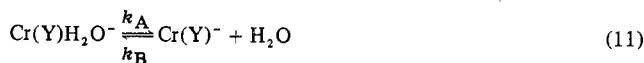
Ligand	$k_1, \text{M}^{-1} \text{s}^{-1}$	k_{-1}, s^{-1}	$10^{-8}k_2, \text{M}^{-2} \text{s}^{-1}$	K_1 (kin), M^{-1}	K_1 (spec), M^{-1}	$\log K_{\text{HX}}^b$
Cr(VI)	3.2 ± 0.2	0.060	0.14 ± 0.03	53 ± 3	78 ± 15	5.91 ^e
Mo(VI)	21 ± 2	0.46	1.1 ± 0.2	46 ± 4	44 ± 7	3.55 ^f
W(VI)	27 ± 4	1.50	0.50 ± 0.30	18 ± 3	24 ± 2	$\sim 3.5^g$
Azide ^c	98 ± 5	13.4	0.0021 ± 0.0012	7.3 ± 0.6	5.9 ± 0.3^d	4.34
Acetate ^{e,d}	3.3 ± 0.4	5.4 ± 0.6	0.0019 ± 0.0002		0.62 ± 0.03	4.59 ^h

^a $k_{-1} = k_1/K_1$. ^b K_{HX} is the protonation constant (M^{-1}) for X^{n-} . ^c $I = 1.0 \text{ M}$ (NaClO_4). ^d Reference 10. ^e Y. Sasaki, *Acta Chem. Scand.*, **16**, 719 (1962); $I = 3.0 \text{ M}$ (NaClO_4), 25 °C. ^f J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, **3**, 735 (1964); $I = 1.0 \text{ M}$ (NaCl), 25 °C. ^g K. B. Yatsimirskii and K. E. Prik, *Zh. Neorg. Khim.*, **9**, 1838 (1964); 25 °C. ^h S. Ahrlund, *Acta Chem. Scand.*, **5**, 199 (1951); $I = 1.0 \text{ M}$ (NaClO_4), 20 °C.

group compared to H_2O . Similarly the less prominent k_2 term in (8) most likely corresponds to the reactant pair as in (10).



We now consider the mechanism of k_1 . It is clear from a comparison of results obtained for $\text{Cr}^{\text{III}}\text{-MED3A}$ that the free carboxylate arm of $\text{Cr}^{\text{III}}\text{-EDTA}$ promotes rapid ligand substitution at $\text{Cr}(\text{III})$. It is presumably able to do this by transient coordination with labilization of the H_2O . Since this will give a seven-coordinate intermediate *before* bond formation to the incoming ligand can be effective and it does not seem reasonable to invoke an eight-coordinate intermediate, we conclude that reaction occurs in two stages, eq 11 and 12.



The complex $\text{Cr}(\text{Y})^-$ is a transient species in which the EDTA is sexadentate. Since the first step k_A is an intramolecular associative process, by the principle of microscopic reversibility k_B must be also. It is probable that k_C is a similar kind of reaction to k_B and on this basis there is a case for k_C and k_D being associative. Now if we assume that the steady-state approximation applies to $\text{Cr}(\text{Y})^-$, we obtain (13). Since k_{eq}

$$k_{\text{eq}} = \frac{k_A k_C [\text{X}^{n-}]}{k_B + k_C [\text{X}^{n-}]} + k_D \quad (13)$$

is strictly first order in $[\text{X}^{n-}]$ in all cases, the limiting condition $k_B \gg k_C [\text{X}^{n-}]$ must apply. It follows that $k_1 = k_A k_C / k_B$, where k_A/k_B is common to all reactions studied and k_C varies as the identity of X^{n-} is varied. Attempts have been made previously to detect the sexadentate species,³ without success. No temperature-jump relaxation process (time range 10 μs –50 ms) corresponding to reaction 11 was detected in this work, λ 350–650 nm, with $3 \times 10^{-3} \text{ M}$ solutions of the $\text{Cr}^{\text{III}}\text{-EDTA}$ complex at pH 5.21.

With (11) and (12) in mind it is appropriate to consider whether values of k_1 and k_{-1} , Table VII, support an associative mechanism for k_C and k_D as suggested. An $\text{S}_{\text{N}}1$ nonlimiting process would predict that for reactants X^{n-} of the same charge, k_1 would be invariant (at least within a factor of 3). This is not the case with azide and acetate where k_1 for azide is 30 times that for acetate. Azide moreover is known to be a good nucleophile and an associative process would therefore seem more reasonable. The k_{-1} values for 2- reactants parallel the basicities suggesting that bond breaking is of some importance. A nonlimiting $\text{S}_{\text{N}}2$ (or I_a) process is consistent with the data at present available.

We turn now to the k_2 term which even under the most favorable conditions investigated makes only relatively small ($\leq 25\%$) contributions. Ogino et al. have found that the uncoordinated ethylhydroxy group of the $\text{Cr}(\text{III})$ complex with *N*-hydroxyethylethylenediamine-*N,N',N'*-triacetate produces a labilization of the aquo ligand comparable to that of the free

Table VIII. Ratios of Rate Constants ($\text{M}^{-1} \text{s}^{-1}$) for the Complexing of $\text{HX}^{(n-1)-}$ to $\text{Cr}(\text{Y})\text{H}_2\text{O}^-$ (k_2/K_{HX}) and of X^{n-} to $\text{Cr}(\text{Y})\text{H}_2\text{O}^-$ (k_1) at 25 °C, $I = 1.00 \text{ M}$ (LiClO_4)

Ligand	$k_2/k_1 K_{\text{HX}}$	Ligand	$k_2/k_1 K_{\text{HX}}$
Cr(VI)	4	Azide	0.1
Mo(VI)	1200	Acetate	1.5
W(VI)	~ 500		

carboxylate.¹⁰ They have accordingly interpreted the k_2 term for acetate as a labilization effect directly attributable to the protonated free carboxylate group. This requires that $-\text{CO}_2\text{H}$ is 10^3 times more effective than $-\text{CO}_2^-$. A difference in reactivity of this order of magnitude is difficult to accept, and certainly for an associative process we would expect $-\text{CO}_2^-$ to be much more effective. This is as observed in the quadridentate \rightarrow quinquedentate $\text{Cr}^{\text{III}}\text{-EDTA}$ interconversion, when $-\text{CO}_2^-$ is ca. 10^2 times more effective.¹¹ The mechanism (12)–(13) provides an alternative explanation if the k_1 and k_2 terms are directly attributable to reactions involving X^{n-} and $\text{HX}^{(n-1)-}$, protonation constant K_{HX} . Rate constants k_2/K_{HX} are comparable to k_1 for $\text{Cr}(\text{VI})$, azide, and acetate. For $\text{Mo}(\text{VI})$ and $\text{W}(\text{VI})$ however k_2/K_{HX} is much bigger than k_1 (factor of ca. 10^3), Table VIII. Proton transfer from $\text{HX}^{(n-1)-}$ to the departing $-\text{CO}_2^-$ may be relevant, thus helping to explain why k_2 is not effective in the reaction of the ethylhydroxy-substituted EDTA complex with acetate.¹⁰

The interpretation that in the present work the attached carboxylate $-\text{CO}_2^-$ replaces X^{n-} (k_D) in an associative process is of considerable interest. The case for an $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanism in the slow interconversion of quinquedentate and sexadentate $\text{Co}^{\text{III}}\text{-EDTA}$ complexes is not as clear-cut, and both mechanisms have been considered.¹³ Direct replacement of negative ligands is not observed in other instances, e.g., the reaction of $\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$ with NCS^- ,¹⁴ since ion pairing to the incoming ligand is electrostatically more favorable on the remote side of the complex. For an adjacent (attached) carboxylate clearly direct replacement of a negative ligand is possible. A currently acceptable view is that chromium(III) (t_{2g}^3) is more readily able to utilize an associative pathway than cobalt(III) (t_{2g}^6). The mechanism involved for quinquedentate EDTA complexes may differ therefore for chromium(III) and cobalt(III).

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Registry No. $\text{Cr}(\text{EDTA})\text{H}_2\text{O}^-$, 19610-17-4; CrO_4^{2-} , 13907-45-4; MoO_4^{2-} , 14259-85-9; WO_4^{2-} , 14311-52-5; N_3^- , 14343-69-2.

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Reactions of Coordinated Molecules. 6. Preparation of Tris-Chelate Complexes Containing Metallo- β -diketonate Ligands

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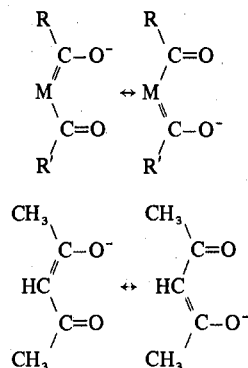
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The nucleophilic addition of a lithium reagent, $R'Li$, to a carbon monoxide ligand of an acyl complex, $RC(O)M(CO)_5$, where M is manganese or rhenium affords a *cis*-diacylmetalate anion, *cis*-(RCO)($R'CO$) $M(CO)_4^-$. These anions are metallo analogues of the enolate anions of 1,3-diketones. This similarity is demonstrated by the coordination of these anions to the central metal ions Al(III) and Ga(III) forming neutral tris-chelate complexes. The preparation of ten such complexes which contain metallo analogues of acetylacetonate, propionylacetonate, isobutyrylacetonate, phenylacetylacetonate, dimethylcarbamylacetonate, valerylacetonate, carboethoxyacetonate, and valerylisobutyrylmethanide as ligands is reported. The solution infrared spectra of these complexes are discussed and the solution proton magnetic resonance spectra indicate *cis*-*trans* isomerization for several of the complexes containing unsymmetrical metallo- β -diketonate ligands.

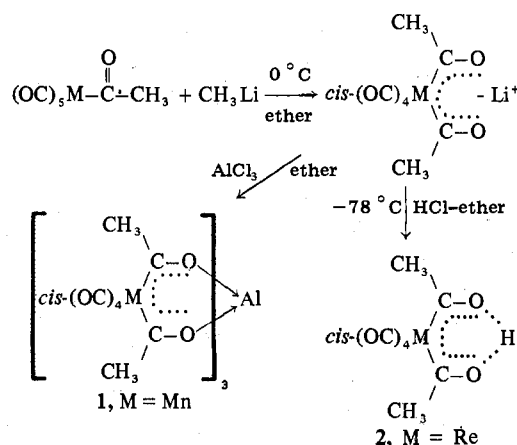
Introduction

During the last 7 years there have been three reports of the preparation of diacylmetalate anions of the type *cis*-[[$RC(O)$][$R'CO$]] M^{n-} , where M is a transition metal atom having ancillary ligands and R and R' are alkyl or aryl groups.¹⁻³ We realized that these anions are isoelectronic with the acetylacetonate anion (where R and R' are methyl), and we initiated an investigation of a possible similarity in reaction chemistry.



Recently we reported such a similarity in both the coordination chemistry⁴ and the acid-base behavior⁵ of the "metalloacetylacetonate" anion to that of the acetylacetonate anion as shown below.

The x-ray crystallographic structure of the tris-chelate complex **1** and of the protonated anion **2** revealed that the "metalloacetylacetonate" anion coordinates to aluminum as a bidentate chelate affording a complex which is essentially isostructural to $Al(acac)_3$ and that the conjugate acid of the "metalloacetylacetonate" anion exists in the solid state as the symmetrical enol tautomer as found for tetraacetyethane.⁶



We wish to report now the synthesis and characterization of several tris-chelate coordination complexes containing solely "metallo- β -diketonate" molecules as ligands. These complexes are formally derivatives of complex **1** where M is Mn or Re, the central metal ion is Al(III) or Ga(III), and either one or both of the methyl substituents are replaced by other groups.

Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen at $25^\circ C$. Diethyl ether and tetrahydrofuran were dried over Na/K alloy under a nitrogen atmosphere. Other solvents were dried over 4 Å molecular sieves and were purged with nitrogen before use. Manganese and rhenium carbonyl dimers were purchased from Pressure Chemical Co. (Pittsburgh, Pa.). Anhydrous gallium trichloride was purchased from Ventron Corp. and was handled under a nitrogen atmosphere in a glovebag.

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer as cyclohexane solutions in 0.10-mm sodium chloride cavity cells using