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Chromium(II) Reduction of Malonatotetraamminecobalt(III) and Tris(malonato)cobaltate(III)

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The malonatotetraamminecobalt(III) complex $[Co(NH_3)_4(C_3H_2O_4)]ClO_4$ has been prepared and characterized by elemental analyses and ir and uv–visible spectra. Consistent with a chelated structure, aquation takes place in two stages, the first stage exhibiting a first-order dependence on $[H^+]$; $k_0 = 3.15 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25°. Reduction by Cr^{2+} gives >87% of the chelated product $Cr(H_2O)_4(C_3H_2O_4)^+$, and at 25°, $I = 1.0\ M$ ($LiClO_4$), $k_1 = 26.4\ M^{-1}\ sec^{-1}$, $\Delta H_1^‡ = 7.22 \pm 0.26$ kcal mol^{-1}, and $\Delta S_1^‡ = -27.8 \pm 0.9$ cal K^{-1} mol^{-1}. The Cr^{2+} reduction of tris(malonato)cobaltate(III) gives both chelated and monodentate products, $Cr(H_2O)_4(C_3H_2O_4)^+$ and $Cr(H_2O)_5(C_3H_3O_4)^{2+}$, the ratio of the two being dependent on $[H^+]$. Thus, with $[H^+] = 0.02\ M$, 56% and 31%, respectively, of these forms were identified, whereas at $[H^+] = 0.6\ M$, 15% and 68% were obtained. No chromium(III) product having more than one malonate ligand was identified. The reaction of Cr^{2+} with $Co(C_3H_2O_4)_3{}^{3-}$ was too fast to follow using the stopped-flow technique $k > 10^6\ M^{-1}\ sec^{-1}$ at 2°, $I = 1.0\ M$ ($LiClO_4$).

Although the Cr^{2+} reductions of malonatopentaamminecobalt(III),[1] oxalatopentaamminecobalt(III),[2] oxalatotetraamminecobalt(III),[3] and tris(oxalato)cobaltate(III)[4] have been investigated, corresponding studies on the reductions of malonatotetraamminecobalt(III) and tris(malonato)cobaltate(III) complexes have not been reported. The latter are of interest since chelated malonate provides exposed nonsterically hindered carbonyl centers for Cr^{2+} attack.[5] There is also the possibility that the chromium(III) product from the reduction of tris(malonato)cobaltate(III) might contain two malonate ligands, since the Cr^{2+} reduction of tris(oxalato)cobaltate(III) produces a bis(oxalato)chromate(III) species. A chromium(III) product containing chelated malonate was at the outset considered less likely, because of the remoteness of the carbonyl oxygens from each other.

Experimental Section

Preparation and Characterization of the Malonatotetraamminecobalt(III) Complex. Carbonatotetraamminecobalt(III) was first prepared as the perchlorate salt by the method described by Siebert and Scheidermaier.[6] This was converted to the malonatotetraamminecobalt(III) complex by stirring (8 g) with a slight excess of malonic acid (3 g, B.D.H. Technical Reagent grade), in 30 ml of water at 70° until there was no further effervescence. The solution was filtered and then cooled in ice. The crystals were collected, washed with ethanol, and dried in air. These were recrystallized by dissolving in water at 30°, adding a solution of $LiClO_4$ (3.5 *M*), and cooling. The crystals which separated were washed with ethanol. As a precautionary measure samples were stored over P_2O_5 in vacuo to prevent absorption of moisture and subsequent hydrolysis. Anal. Calcd for $[Co(NH_3)_4(C_3H_2O_4)]ClO_4$: C, 10.9; H, 4.3; N, 17.0; Cl, 10.8. Found: C, 10.8; H, 4.2; N, 16.5; Cl, 11.1. There was no loss of weight when the complex was left over P_2O_5 in vacuo for several days, which is consistent with the formula $[Co(NH_3)_4(C_3H_2O_4)]ClO_4$ with no water molecules of crystallization. Ir spectra of solid samples using KBr disks gave bands as expected for coordinated malonate, with no band at ca. 1750 cm^{-1}, the wave number characteristic of a free –COOH group. A diffuse-reflectance spectrum of the perchlorate salt gave peaks at 518 (±3) and 362 (±4) nm. The complex is stable for ca. 45 min when dissolved in water or $LiClO_4$ solution (pH ca. 5) at room temperature, and the uv–visible spectrum gives maxima at 519 nm (ϵ 88.6 M^{-1} cm^{-1}) and 364 nm (ϵ 54.7 M^{-1} cm^{-1}). It is concluded that the chelated structure persists in neutral solution for a substantial period. When the complex is dissolved in aqueous solutions, pH <1, aquation is observed (see Results).

Kopple and Miller[7] have previously reported the preparation of a complex believed to be $Co(NH_3)_4(C_3H_2O_4)^+$, but the spectrum [λ_{max} 510 (ϵ 70 M^{-1} cm^{-1}), λ_{max} 360 (ϵ 78 m^{-1} cm^{-1})] is different from that which we have obtained. Their observations were on a solution isolated by ion exchange from a mixture containing some trans-disubstituted product. The complex was shown to be eluted at the same rate as $Co(NH_3)_4(H_2O)(O_2CCH_3)^{2+}$ even though the latter is 2+ charged. They did not isolate a solid sample, and lack of correspondence between their data and those reported here suggests that they were dealing with a different complex. Thus they reported that their complex was stable to aquation in contrast with the fairly rapid ring-opening process observed in the aquation of our complex. They also investigated the Cr^{2+} reduction, and again their results are not in complete agreement with those reported in this paper. The possible formation of a cis-disubstituted complex under the reaction conditions of Kopple and Miller cannot be ruled out.

Preparation of Tris(malonato)cobaltate(III). The preparation and characterization of $K_3[Co(C_3H_2O_4)_3]\cdot 4H_2O$ have been reported previously.[8,9] Sulfab and Al-Obadie[10] have investigated the hydrogen ion dependent decomposition to give Co^{2+} at 25°, and preliminary results indicate a rate (*M* sec^{-1}) as in (1). The complex is reported[8] to be unstable to daylight, and solutions were prepared with the exclusion of light. Solutions in neutral $LiClO_4$ at 0° gave no change in absorbance at 350–700 nm over 30 min.

$$\text{rate} = 6.3 \times 10^{-2}\,[H^+][Co(III)] + 2.45 \times 10^{-1}\,[H^+]^2[Co(III)] \qquad (1)$$

Other Reactants. Solutions of hexaaquochromium(II) perchlorate, typically $[Cr^{2+}]$ = ca. 0.45 *M* with $[HClO_4]$ = ca. 0.6 *M*, were prepared by cathodic reduction of hexaaquochromium(III) perchlorate. The latter was prepared by dissolving CrO_3 (B.D.H. Analar) in perchloric acid and reducing to the III state with H_2O_2. Platinum black was added to ensure overnight decomposition of excess H_2O_2. Perchloric acid (72%, Analar grade, B.D.H.) was used. Lithium perchlorate was prepared by addition of lithium carbonate to perchloric acid. The product was recrystallized until free from anion impurities. A sample of *cis*-$[Co(NH_3)_4(H_2O)_2](ClO_4)_3$ was prepared by the method described by Linhard and Weigel.[11]

Determination of Products by Ion Exchange. Solutions containing Cr^{2+}, $HClO_4$, and $LiClO_4$ as required were syringed onto deoxygenated samples of the cobalt(III) complex. The complex $Co(NH_3)_4(C_3H_2O_4)^+$ was present as a solid or in aqueous solution (freshly prepared), and $Co(C_3H_2O_4)_3{}^{3-}$ was present as the solid. Flasks containing $Co(C_3H_2O_4)_3{}^{3-}$ were covered with Al foil to exclude light. Reactant concentrations were ca. 10^{-2} *M* with $[H^+]$ in the range 0.01–0.60 *M*, $I = 1.0\ M$ ($LiClO_4$), and the temperature ca. 20°. Potassium perchlorate was precipitated in the case of $Co(C_3H_2O_4)_3{}^{3-}$. After allowing 15 min for reaction to occur, flasks were opened to the atmosphere, and the contents diluted fivefold with ice-cold water. At this point the $KClO_4$ redissolved. The resultant solutions at $I = 0.2\ M$ and 0° were passed down a column of Dowex 50W-X2 (200–400 mesh) resin in the H^+ form at 0°. Elution of a blue-mauve band (1+ charge) commenced on loading the solutions and was completed using 0.2 *M* $HClO_4$. The band was analyzed for chromium content (see below) and from details of the visible absorption spectrum was identified as $Cr(H_2O)_4(C_3H_2O_4)^+$, Table I. A second (blue) band was obtained with $Co(C_3H_2O_4)_3{}^{3-}$ but not with $Co(NH_3)_4(C_3H_2O_4)^+$. This band was eluted with 0.2 *M* $HClO_4$–0.5 *M* $LiClO_4$, analyzed for chromium, and from its spectrum identified as Cr-

Table I. Comparison of Uv-Visible Absorption Spectra of Chromium(III) Products with Values Previously Reported

Complex	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	Ref
$Cr(H_2O)_4(C_3H_2O_4)^+$	566 (±1)	31.0 (±0.2)	418 (±0)	27.4 (±0.4)	This work[a]
	559	31.4	415	26.1	12
	559	31.3	412	25.2	18
	559	32.4	416	27.2	*b*
	557	31.0	409	26.0	*c*
$Cr(H_2O)_5(C_3H_3O_4)^{2+}$	570 (±0)	23.7 (±0.4)	412 (±1)	22.7 (±0.6)	This work[d]
	568	25.6	412	23.4	12
	571	24.4	410	23.7	18
$Cr(H_2O)_6^{3+}$	575 (±2)	~14	410 (±2)	~17	This work[e]
	574	13.3	408	15.8	*f*

[a] Values averaged from four samples obtained from ion-exchange separation of products. [b] R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 5569 (1958). [c] E. Mantovani and C. Furlani, *Z. Anorg. Allg. Chem.*, **364**, 322 (1969). [d] Values averaged from three samples: two obtained from Cr^{2+} reduction of $Co(C_3H_2O_4)_3^{3-}$ and one from the procedure described in ref 12. [e] Samples too dilute for accurate measurements. [f] E. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968).

$(H_2O)_5(C_3H_3O_4)^{2+}$, Table I. A pink band of Co^{2+} was eluted with 0.5 M $HClO_4$–0.5 M $LiClO_4$ and analyzed for cobalt (see below). A small diffuse band of charge 3+ was finally eluted with 1.0 M $HClO_4$–0.5 M $LiClO_4$ and shown to correspond to $Cr(H_2O)_6^{3+}$. Traces of green chromium(III) dimeric species were generally observed at the top of the column, but these were not eluted.

To confirm the product identification, both the malonatochromium(III) complexes $Cr(H_2O)_4(C_3H_2O_4)^+$ and $Cr(H_2O)_5(C_3H_3O_4)^{2+}$ were prepared by the procedure described by Huchital and Taube,[12] using Fe^{3+}, malonic acid, perchloric acid, and Cr^{2+}. The ion-exchange behavior, spectra, and stability of the chromium(III) complexes so prepared confirmed the assignments made to the products obtained in the Cr^{2+} reductions of $Co(NH_3)_4(C_3H_2O_4)^+$ and $Co(C_3H_2O_4)_3^{3-}$. Solutions of chromium(III) were determined as chromium(VI), and solutions of cobalt(II) as $CoCl_4^{2-}$ or $CoCl_3H_2O^-$ by standard procedure.[13]

Procedure for Kinetic Experiments. A Durrum-Gibson stopped-flow spectrophotometer was used to study the Cr^{2+} reductions. Solutions of the cobalt(III) complexes were prepared in 1 M $LiClO_4$ and were deoxygenated by bubbling N_2 through for ca. 20 min. Some 15–20 min was allowed subsequently for thermostating. Solutions of $Co(C_3H_2O_4)_3^{3-}$ were kept at ice temperature and were covered with Al foil to exclude light. Conventional spectrophotometric studies were carried out using Unicam SP500 and SP800 instruments.

Runs on the aquation of the malonatotetraamminecobalt(III) complex were initiated by mixing equal volumes of $Co(NH_3)_4(C_3H_2O_4)^+$ (in water) and $HClO_4$ or $LiClO_4$ at 25° to give $I = 1.0$ M. The aquation was monitored at 516 nm over the range $[H^+] = 0.05–1.0$ M. Plots of log $(A_t - A_\infty)$ against time were linear to >95% completion, and rate constants k_a were obtained from the slopes (×2.303). Values of A_∞ were as recorded when the absorbance was constant for ca. 2 hr. Absorbance (A_0) readings from the first-order plots extrapolated to $t = 0$ were as expected for $Co(NH_3)_4(C_3H_2O_4)^+$. The same solutions were also mixed on the stopped-flow spectrophotometer to confirm that no initial rapid change was occurring.

Results

Aquation of Malonatotetraamminecobalt(III). Rate constants 10^3k_a (sec^{-1}) were 1.12, 7.05, and 31.8 at $[H^+] = 0.05$, 0.25, and 1.00 M, respectively, giving a satisfactory fit to (2),

$$k_a = k_0[H^+] \tag{2}$$

with $k_0 = 3.15 \times 10^{-2}$ M^{-1} sec^{-1} at 25°, $I = 1.0$ M ($LiClO_4$).

Absorbance readings A_∞ were too high to correspond to the formation of *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$, the spectrum of which is well documented: λ_{max} 506 nm (ϵ 48 M^{-1} cm^{-1}), λ_{max} 357 nm (ϵ 39 M^{-1} cm^{-1}).[14] The latter has also been determined independently in this work: λ_{max} 506 nm (ϵ 51 M^{-1} cm^{-1}), λ_{max} 357 nm (ϵ 39 M^{-1} cm^{-1}). The product, believed to be *cis*-$Co(NH_3)_4(H_2O)(C_3H_3O_4)^{2+}$, gave λ_{max} 508 nm (ϵ 65 M^{-1} cm^{-1}) and λ_{max} 357 nm (ϵ 50 M^{-1} cm^{-1}) and is remarkably similar to other cis complexes containing aquo and carboxylato ligands, e.g., $Co(NH_3)_4(H_2O)(O_2CCH_3)^{2+}$: λ_{max} 510 nm (ϵ 67 M^{-1} cm^{-1}), λ_{max} 355 nm (ϵ 50 M^{-1} cm^{-1}).[7] Further spectrophotometric changes at 516 nm were observed over a period of many days, $t_{1/2}$ = 10 days, when the spectrum approached more closely that of *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$. The rate constant $<10^{-6}$ sec^{-1} indicated in these experiments for the second stage of the aquation is in keeping with known behavior of, e.g., $Co(NH_3)_5(O_2CCH_3)^{2+}$, which aquates extremely slowly, rate constant 1.6×10^{-8} sec^{-1} at 25°.[15]

Table II. Results of Product Separation for the Reaction of Cr^{2+} with $Co(NH_3)_4(C_3H_2O_4)^+$ at ~20°, $I = 1.0$ M ($LiClO_4$)

Reactants			Products			
10^2 $[Cr^{2+}]$, M	10^2 [Co(III)], M	$[H^+]$, M	$Cr(H_2O)_4(C_3H_2O_4)^+$ [a]	$Cr(H_2O)_6^{3+}$ [a]	$Cr(III)_T$ [a,b]	Co^{2+} [c]
0.79	0.72[d]	0.01	0.88	0.06	0.94	0.88
0.79	0.75	0.01	0.86	0.07	0.93	0.86
1.00	0.97[d]	0.02	0.88	0.05	0.93	0.89
1.06	1.00	0.02	0.86	0.07	0.93	0.93
1.06	1.00	0.10	0.87	0.07	0.94	0.93
0.53	0.66	0.11	0.85	*e*		0.88
1.05[f]	0.55	0.11	0.87	0.06	0.93	0.88
5.05	5.00	0.19	0.95	0.01	0.96	0.86
1.06	1.00	0.60	0.87	0.14	1.01	0.90
5.05	1.00	0.60	0.89	0.03	0.92	0.88

[a] Expressed as fraction of Co^{2+} recovered. [b] Total Cr(III) recovered. [c] Expressed as fraction of Co(III) reactant. [d] Cr^{2+} was added to solid; elsewhere Co(III) was in solution before adding Cr^{2+}. [e] $Cr(H_2O)_6^{3+}$ not separated from excess Co(III). [f] Excess Cr^{2+} oxidized by atmospheric O_2 to give Cr^{III}_2 which was not eluted.

The ion-exchange behavior of a sample of *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$ was compared with that of the initial product obtained in the aquation of $Co(NH_3)_4(C_3H_2O_4)^+$ using Dowex 50W-X12 (200–400 mesh). The initial product obtained on allowing 1.6×10^{-3} M $Co(NH_3)_4(C_3H_2O_4)^+$, $[H^+] = 0.25$ M, to aquate for 30 min moved off the column prior to *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$ and is assigned a 2+ charge, consistent with the formula $Co(NH_3)_4(H_2O)(C_3H_3O_4)^{2+}$.

Products of the Cr^{2+} Reduction of $Co(NH_3)_4(C_3H_2O_4)^+$. Details of visible absorption spectra of chromium(III) complexes are given in Table I. Results of ion-exchange experiments are summarized in Table II. The fraction of $Cr(H_2O)_4(C_3H_2O_4)^+$ recovered is not affected by $[H^+]$ or by the ratio of reactants suggesting that the chelate species is produced by the Cr^{2+} reduction of $Co(NH_3)_4(C_3H_2O_4)^+$ and not as a result of secondary reactions with excess Cr^{2+}. No variation in results was observed when the Cr^{2+} was allowed to react with the solid complex, thus supporting the belief that the cobalt(III) complex retains its chelated structure in solution. About 7% of $Cr(H_2O)_6^{3+}$ is produced, but the amount shows considerable variation and may result from side reactions. The upper limit set by the results for the fraction of $Cr(H_2O)_5(C_3H_3O_4)^{2+}$ formed is ≤7% and none was identified on the column.

Kinetics of the Cr^{2+} Reduction of $Co(NH_3)_4(C_3H_2O_4)^+$. The Cr^{2+} reactant was in large excess. Absorbance changes were monitored at 520 nm by stopped-flow spectrophotometry. Plots

Table III. Pseudo-First-Order Rate Constants for the Cr^{2+} [a] Reduction of the $Co(NH_3)_4(C_3H_2O_4)^+$ [b] Complex [$I = 1.0\ M$ ($LiClO_4$)]

Temp, °C	$[H^+]$, M	k_{Cr}, sec^{-1}	Temp, °C	$[H^+]$, M	k_{Cr}, sec^{-1}
25.4	0.01	0.189[c]	25.4	0.20	2.09
	0.49	0.182		0.20	2.84[c]
	0.47	0.254[c]	30.1	0.40	0.173[c]
	0.30	0.278[c]		0.47	0.343[c]
	0.05	0.286		0.02	0.40
	0.10	0.30		0.20	1.00
	0.20	0.30[c]	35.1	0.47	0.43
	0.20	0.31	37.6	0.01	0.192[c]
	0.20	0.32		0.49	0.196[c]
	0.20	0.42[c]		0.20	0.43
	0.20	0.73[c]		0.20	0.85
	0.12	1.08[c]	40.1	0.47	0.54[c]
	0.36	0.91		0.02	0.56[c]
	0.20	1.34			

[a] $[Cr^{2+}]$ in the range $(0.43-10.4) \times 10^{-2}\ M$. [b] $[Co^{III}]$ in the range $(1.3-7.5) \times 10^{-4}\ M$. [c] Two runs averaged.

of log $(A_t - A_\infty)$ against time were linear to ≥93% completion, and values of A_0 obtained for $t = 0$ were as expected for the $Co(NH_3)_4(C_3H_2O_4)^+$ complex after allowing for the Cr^{2+} absorbance. First-order rate constants k_{Cr}, Table III, showed no dependence on $[H^+]$ or $[Co(III)]$ and gave a first-order dependence on $[Cr^{2+}]$. Values of k_1 as defined in (3) were

$$-d[Co(III)]/dt = k_1[Cr^{2+}][Co(III)] \qquad (3)$$

obtained from graphs of k_{Cr} against $[Cr^{2+}]$. Activation parameters for k_1 were determined by a nonlinear least-squares treatment with weighting factor $1/k_{Cr}^2$.[16] This gave $\Delta H_1^\ddagger = 7.22 \pm 0.26$ kcal mol^{-1}, $\Delta S_1^\ddagger = -27.8 \pm 0.9$ cal K^{-1} mol^{-1}, and $k_1 = 26.4\ (\pm 0.3)\ M^{-1}\ sec^{-1}$ at 25°, $I = 1.0\ M$ ($LiClO_4$).

Products of the Cr^{2+} Reduction of $Co(C_3H_2O_4)_3^{3-}$. Reactions were initiated in all cases by the addition of Cr^{2+} solution to a solid sample of $Co(C_3H_2O_4)_3^{3-}$. Three chromium(III) fractions were obtained following separation on an ion-exchange column, and these were identified from known spectra, Table I. The principal products were $Cr(H_2O)_4(C_3H_2O_4)^+$ and $Cr(H_2O)_5(C_3H_3O_4)^{2+}$, Table IV, more of the latter being obtained at higher $[H^+]$. Small amounts of $Cr(H_2O)_6^{3+}$ were again obtained but most likely resulted from side reactions.

Frank and Huchital[17] have reported that $Cr(H_2O)_5(C_3H_3O_4)^{2+}$ may be prepared by the reaction of Cr^{2+} with $Co(C_3H_2O_4)_3^{3-}$, but the short abstract gives no details of their procedure. If their reaction conditions were $[H^+] > 0.6\ M$, it may be that they obtained very little chelated chromium(III) complex. They did not however report that any such species was obtained.

Kinetics of the Cr^{2+} Reduction of $Co(C_3H_2O_4)_3^{3-}$. It was shown that the reaction is too fast to observe by the stopped-flow technique, even with low concentrations of Cr^{2+} ($5 \times 10^{-3}\ M$) and at 2°. Two additional reactions were noted with approximate half-lives of 0.1 sec (a decrease in absorbance) and 2.5 sec (an increase in absorbance), and these were independent of $[Cr^{2+}]$ and $[H^+]$ over the range investigated. However absorbance readings from an extrapolation of data indicated that reduction of cobalt(III) was complete at the commencement of this first stage. Both latter stages could moreover be reproduced by mixing solutions of Cr^{2+} and malonate. It is concluded that the reaction of Cr^{2+} with $Co(C_3H_2O_4)_3^{3-}$ is too fast to follow using the stopped-flow technique and that $k > 10^6\ M^{-1}\ sec^{-1}$. The nature of the Cr^{2+} reduction of free malonate was not investigated further. With an excess of $Co(C_3H_2O_4)_3^{3-}$, when free malonate is unlikely to react appreciably with Cr^{2+}, the same product distribution was (within experimental error) obtained, Table IV.

Reaction of Cr^{2+} with $Cr(H_2O)_5(C_3H_3O_4)^{2+}$. The possibility that Cr^{2+} may catalyze the ring closure of the monodentate malonato complex $Cr(H_2O)_5(C_3H_3O_4)^{2+}$ and that this reaction might account for the production of the chelated complex $Cr(H_2O)_4(C_3H_2O_4)^+$ is now considered. This would require that the closure reaction has a rate constant $\geq 25\ M^{-1}\ sec^{-1}$ at 25°. Samples of $Cr(H_2O)_5(C_3H_3O_4)^{2+}$ were as obtained from the reaction of Cr^{2+} with $Co(C_3H_2O_4)_3^{3-}$ by ion-exchange separation of the products. Reactant concentrations were $[Cr(H_2O)_5(C_3H_3O_4)^{2+}] = 2.14 \times 10^{-3}\ M$, $[Cr^{2+}] = 0.01-0.05\ M$, and $[H^+] = 0.28-0.55\ M$. No absorbance changes were observed at 545 nm on mixing on the stopped-flow apparatus. By conventional spectrophotometry absorbance charges could be monitored for periods of 1–3 hr at 25°. The total change in absorbance was as calculated for the chelation reaction. A further increase in absorbance was observed over the next 24 hr. The latter effect is most likely the result of aquation of the malonato complex followed by reaction of the released ligand with Cr^{2+}. It was concluded that the Cr^{2+}-catalyzed ring closure of $Cr(H_2O)_5(C_3H_3O_4)^{2+}$ is probably $>10^2$ times slower than the reaction of Cr^{2+} with $Co(NH_3)_4(C_3H_2O_4)^+$ and is not effective therefore in that system. It may be assumed that the chelated complex $Cr(H_2O)_4(C_3H_2O_4)^+$ is a primary product of the reduction of $Co(NH_3)_4(C_3H_2O_4)^+$. This assumption finds indirect support in the observation of the products of the Cr^{2+} reduction of $Co(C_3H_2O_4)_3^{3-}$. In this case both chelated and monodentate chromium(III) species are produced, suggesting that Cr^{2+}-catalyzed ring closure of the monodentate malonato complex is ineffective.

The spontaneous ring closure of $Cr(H_2O)_5(C_3H_3O_4)^{2+}$ has previously been shown to occur only very slowly in acidic solutions.[18] Equilibration of the two forms requires ca. 50 hr at 25°.

Discussion

The malonatotetraamminecobalt(III) complex, $Co(NH_3)_4(C_3H_2O_4)^+$, has been prepared for the first time and characterized by elemental analysis and ir and uv–visible spectra. The complex is stable to aquation in neutral solution but ring opening is induced by H^+ ions. Under the latter condition aquation takes place in two stages, which supports

Table IV. Results of Product Separation for the Reaction of Cr^{2+} with $Co(C_3H_2O_4)_3^{3-}$ at ~20°, $I = 1.0\ M$ ($LiClO_4$)

Reactants			Products				
$10^2[Cr^{2+}]$, M	$10^2[Co^{III}]$, M	$[H^+]$, M	$Cr(H_2O)_4$-$(C_3H_2O_4)^+$ [a]	$Cr(H_2O)_5$-$(C_3H_3O_4)^{2+}$ [a]	$Cr(H_2O)_6^{3+}$ [a]	$Cr(III)_T$ [a,b]	Co^{2+} [c]
1.06	1.05	0.02	0.56	0.31	0.03	0.90	1.00
1.06	1.05	0.10	0.25	0.62	0.06	0.93	0.99
1.03	2.06[d]	0.10	0.33[e]	0.58[e]	0.04[e]	0.95	1.04
1.03[f]	0.69	0.10	0.20	0.61	0.09[g]	0.90	1.00
1.06	1.05	0.60	0.15	0.68	0.07	0.90	1.01

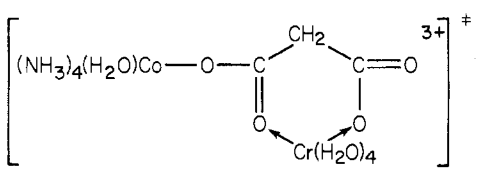
[a] Expressed as fraction of Co^{2+} recovered. [b] Total Cr(III) recovered. [c] Expressed as a fraction of Co(III) reactant. [d] Excess Co(III) undergoes aquation or self-reduction to Co^{2+}. [e] Expressed as fraction of Cr^{2+} reactant. [f] Excess Cr^{2+} oxidized by atmospheric O_2 to give Cr^{III}_2 which was not eluted. The reaction of Cr^{2+} with malonate is a possible contributor. [g] $Cr(H_2O)_6^{3+}$ is probably high because aerial oxidation of excess Cr^{2+} produces a small amount of this species.

the chelated structure. The tris(malonato)cobalt(III) complex, $Co(C_3H_2O_4)_3{}^{3-}$, has been characterized previously.[8,9]

The most striking observations to emerge from the present studies are as follows. The complex $Cr(H_2O)_4(C_3H_2O_4)^+$ containing chelated malonate is the exclusive chromium(III) product of the Cr^{2+} reduction of $Co(NH_3)_4(C_3H_2O_4)^+$ and is formed in substantial amounts along with $Cr(H_2O)_5(C_3H_3O_4)^{2+}$ in the reduction of $Co(C_3H_2O_4)_3{}^{3-}$. It has been demonstrated that the chelated complex is a primary product and is not formed from a reaction of Cr^{2+} with $Cr(H_2O)_5(C_3H_3O_4)^{2+}$. There is no evidence for the transfer of more than one malonate in the Cr^{2+} reduction of $Co(C_3H_2O_4)_3{}^{3-}$. The rate constant for the Cr^{2+} reduction of $Co(NH_3)_4(C_3H_2O_4)^+$ ($k = 26.4\ M^{-1}\ sec^{-1}$ at 25°) is ca. 10^2 times greater than that observed for reduction of $Co(NH_3)_5(CH_3COO)^{2+}$ ($k = 0.35\ M^{-1}\ sec^{-1}$ at 25°)[19] and ca. 10 times greater than observed for reduction of $Co(en)_2(gly)^{2+}$ ($k = 2.2\ M^{-1}\ sec^{-1}$ at 25°).[5] It is however ca. 10^4 times smaller than the rate constant for the Cr^{2+} reduction of $Co(NH_3)_4(C_2O_4)^+$ ($k = 2 \times 10^5\ M^{-1}\ sec^{-1}$ at 25°).[3]

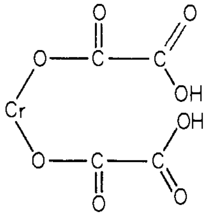
It is important at this stage to consider the stereochemistry of the six-membered malonate ring. Of the three possible strain-free conformations, the boat and chair forms bring the carbonyl oxygens into closest proximity, i.e., on the same side of the ring, and favor chelation of the Cr^{2+} reactant. The carbonyl oxygens are pointing in opposite directions in the "staggered" conformer and are clearly not available for bonding to the same Cr^{2+}. Structures of $(+)_{589}$-$[Cr(C_3H_2O_4)]^{3-}$ [20] and $(+)_{546}$-$[Co(C_3H_2O_4)_2(en)]^-$ [20,21] have been determined and in these complexes the malonate rings take up a nearly planar conformation described as a flattened boat. When other chelate rings are present, intramolecular effects possibly favor this structure, which may explain the observation of Olson and Behnke[18] that Cr^{2+} reduction of $Co(trien)(C_3H_2O_4)^+$ gives monodentate malonatopentaaquochromium(III) as a major product and may also be partly relevant to our own observations with $Co(C_3H_2O_4)_3{}^{3-}$ as oxidant. Rapid interchange involving all possible strain-free conformers may pertain in solution, and conformational changes may of course occur within the precursor complex prior to or at the time of electron transfer. Stretching of cobalt ligand bonds for example is expected to be large since the cobalt(III) oxidant is adding an electron to the σ^* or e_g (antibonding) orbital.

As an alternative to Cr^{2+} bonding initially to both carbonyl oxygens of the chelated malonate, we consider the possibility that Cr^{2+} catalyzes the opening of the ring prior to electron transfer. The Cr^{2+} can then coordinate more readily to the second carbonyl function as in I. The rate constant for Cr^{2+} reduction of $Co(NH_3)_4(C_3H_2O_4)^+$ ($k_2 = 26.4\ M^{-1}\ sec^{-1}$ at 25°) is considerably larger than that for the hydrogen ion catalyzed ring-opening reaction ($k_0 = 3.15 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25°), so that Cr^{2+} must be $\geq 10^3$ times more effective as a catalyst than H^+ for this mechanism to be operative. Ashley and Hamm[23] have demonstrated a relationship between the first formation constants for 2+ metal ion–oxalato complexes and the catalytic rate constants for isomerization, k_i, of *cis* → *trans*-$Cr(H_2O)_2(C_2O_4)_2{}^-$. They postulated a "one-ended" dissociation mechanism for this process assisted by metal ions as well as H^+. Huchital[24] has however studied the Cr^{2+}-catalyzed isomerization and, on the basis of activation parameters, ruled out the "one-ended" dissociation and assigned instead an electron-transfer mechanism. If the "one-ended" dissociation mechanism did apply with $Co(NH_3)_4(C_3H_2O_4)^+$, the 10^3-fold enhancement for Cr^{2+} over H^+ would require a special affinity of Cr^{2+} for the ligand. The Cr^{2+} ion does not appear to exhibit any such behavior toward those ligands for which formation constants have been measured.[25] Thus Cr^{2+} complexes are typically less stable than Cu^{2+} complexes, which seems a good comparison in view of the common Jahn–Teller effect for both these ions.



I

The above discussion applies in the main also to the Cr^{2+} reduction of $Co(C_3H_2O_4)_3{}^{3-}$. Three aspects merit further comment however. The first concerns the rate constant, $k > 10^6\ M^{-1}\ sec^{-1}$ at 2°, for the reduction of this complex. A rapid rate is to be expected by analogy with the Cr^{2+} reduction of $Co(C_2O_4)_3{}^{3-}$, rate constant $4 \times 10^6\ M^{-1}\ sec^{-1}$ at 20°.[4] Both complexes undergo self-reduction to Co^{2+} in their aquation reactions,[8] and both are presumably fairly strong oxidants [$Co(C_2O_4)_3{}^{3-}$; $E_0 = 0.57$ V].[27] An additional factor contributing to the high rate of reduction is the negative charge of the oxidants. The second point concerns the dependence of the product distribution on $[H^+]$. This effect can be explained if at low $[H^+]$ a path involving a doubly chelated transition state gives $Cr(H_2O)_4(C_3H_2O_4)^+$. At high $[H^+]$ protonation of one of the free carbonyl groups, which may be quite extensive for a 3− charged complex, hinders such a path and results in the formation of the monodentate product. An H^+-catalyzed one-ended dissociation of the chelated malonate does not fit the data. If this mechanism were operative, an increase in $[H^+]$ would be expected to assist ring opening and increase the yield of $Cr(H_2O)_4(C_3H_2O_4)$.$^+$ The third aspect which is of interest is the failure to detect any malonatochromium(III) product containing two malonate ligands. When Cr^{2+} reacts with $Co(C_2O_4)_3{}^{3-}$,[4] $Cr(C_2O_4)_3{}^{3-}$,[23] or *cis*- and *trans*-$Cr(H_2O)_2(C_2O_4)_2{}^-$,[23] two oxalate ligands are simultaneously transferred. In the case of $Co(C_2O_4)_3{}^{3-}$ this path is favored at low $[H^+]$, and Huchital has postulated that the initial product of reaction is in all cases a complex as in II. Since no such analogous complex is formed with $Co(C_3H_2O_4)_3{}^{3-}$, it would seem that the steric requirements for a doubly bridged transition state rule out this path.



II

The rate constant for Cr^{2+} reduction of $Co(NH_3)_4(C_3H_2O_4)^+$ ($k_1 = 26.4\ M^{-1}\ sec^{-1}$ at 25°) is ca. 10^2 times greater than for reduction of $Co(NH_3)_5(O_2CCH_3)^{2+}$.[19] As in the case of $Co(en)_2(NH_2CH_2COO)^{2+}$ a rate enhancement of ca. 1 order of magnitude over $Co(NH_3)_5(CH_3COO)^{2+}$ might be expected for the chelate malonate complex since the carbonyl functions are more exposed. It would appear that a further rate enhancement of an order of magnitude is possibly attributable to the fact that Cr^{2+} chelates to $Co(NH_3)_4(C_3H_2O_4)^+$. The rate constant for the reduction of the unprotonated complex $Co(NH_3)_5(C_3H_2O_4)^+$ is ca. $10^3\ M^{-1}\ sec^{-1}$ at 25° in $NaClO_4$ solutions, $I = 4.0\ M$, using an estimate for the acid dissociation constant (K_a = ca. $3.9 \times 10^{-4}\ M^{-1}$)[1a] and assuming deprotonation occurs prior to coordination of the reductant. Larger rate enhancements are also observed when Cr^{2+} chelates to oxalate in $Co(NH_3)_4(C_2O_4)^+$.[3] A more extensive reduction in the energy of acceptor orbitals is believed to result in the case of the α carbonyls of the oxalate. Any interaction of the carbonyls of malonate must occur via the methylene group, and the effect is therefore much less.

In summary we conclude that the data obtained for the reactions of Cr^{2+} with $Co(NH_3)_4(C_3H_2O_4)^+$ and $Co(C_3H_2O_4)_3^{3-}$ are best explained in terms of chelation of Cr^{2+} to a chelated malonate. Protonation of the $Co(C_3H_2O_4)_3^{3-}$ complex is believed to be largely responsible for the decrease in production of the chelated malonatochromium(III) species.

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Registry No. $[Co(NH_3)_4(C_3H_2O_4)]ClO_4$, 54870-19-8; $Co(C_3H_2O_4)_3^{3-}$, 22174-09-0; $Cr(H_2O)_6^{2+}$, 20574-26-9; $Cr(H_2O)_4(C_3H_2O_4)^+$, 23153-91-5; $Cr(H_2O)_5(C_3H_3O_4)^{2+}$, 45095-55-4; $Cr(H_2O)_6^{3+}$, 14873-01-9; *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$, 18460-36-1; *cis*-$Co(NH_3)_4(H_2O)(C_3H_3O_4)^{2+}$, 54870-20-1; carbonatotetraamminecobalt(III) perchlorate, 37549-01-2.

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Kinetics of Reduction of $Co(NH_3)_5Cl^{2+}$ and *cis*- and *trans*-$Co(en)_2Cl_2^+$ by Ti(III)

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The variation of rate with $[H^+]$ for reduction of three Co(III) oxidants by Ti(III) yields the following second-order rate constants (M^{-1} sec^{-1}, 25.2°) for reduction by $TiOH^{2+}$ and Ti^{3+}: $Co(NH_3)_5Cl^{2+}$, 0.48, <0.001; *cis*-$Co(en)_2Cl_2^+$, 0.75, 0.002; *trans*-$Co(en)_2Cl_2^+$, 2.8, 0.009. The influence of geometry of the oxidant is less than that expected on the basis of related systems.

Although Ti^{3+} is widely used analytically as an inorganic reductant, the rates of only a few of its redox reactions with Co(III) oxidants have been studied, perhaps partially because Ti^{3+} reduces ClO_4^-, the usual medium anion for such reactions. However, this reaction itself indicates that the electron-donor properties of Ti^{3+} are unusual and may be of special interest in understanding fundamental aspects of redox processes. We now report a study of Ti^{3+} reductions of three simple Co(III) oxidants.

Experimental Section

Preparation of Co(III) Complexes. $(Co(NH_3)_5Cl)Cl_2$[2] and *trans*- and *cis*-$(Co(en)_2Cl_2)Cl$[3] were prepared according to literature methods and recrystallized twice from 10^{-3} *M* HCl. Uv-visible spectra agreed with literature values.[4-6] $Co(NH_3)_5Cl(Tos)_2$ (Tos^- = *p*-toluenesulfonate anion) was prepared by dissolving the chloro salt in 40 times its weight of warm (80°) 0.1 *M* HTos, filtering, adding solid HTos to make the filtrate ~1 *M* in HTos, and cooling. The precipitate was recrystallized twice from 0.1 *M* HTos, washed with ethanol and ether, and dried at 100° for 2 hr.

Anal. Calcd: Co, 11.29; Cl, 6.79; C, 32.22; N, 13.42; S, 12.29; H, 5.60. Found: Co, 11.34; Cl, 6.68; C, 32.73; N, 13.50; S, 12.21; H, 5.72.

Preparation of Ti(III) Solutions. All manipulations of Ti(III) solutions were performed under anaerobic conditions using N_2 atmosphere. Ti(III) solutions were prepared in three different media: chloride, trifluoromethanesulfonate, and *p*-toluenesulfonate. For the two former media, titanium metal (Alfa Inorganics m3N+ sponge) was dissolved in 3 *M* acid by heating at 50–60° for 24–48 hr. The resulting stock solutions, 0.5–0.7 *M* in Ti(III), were filtered and stored at 1°. For *p*-toluenesulfonate media, titanium metal was first dissolved in a similar way in 2 *M* sulfuric acid, sulfate ion was precipitated with a 5% excess of barium *p*-toluenesulfonate, and the solution was centrifuged, filtered, and stored at 1°. Attempts were made to prepare a concentrated titanium(III) *p*-toluenesulfonate solution from sulfate solutions by using the Tos^- form of a strongly basic anion-exchange resin column (Fisher Rexyn 201) or of a weakly acidic cation-exchange resin column (Fisher Rexyn 102). However, Ti(III) reacted with both resins.

Diluted stock solutions of Ti(III) were standardized by oxidation to Ti(IV) with excess of chromium(VI), followed by addition of an excess of iron(II) and back-titration with chromium(VI) in ~1 *M* H_2SO_4 using *N*-phenylanthranilic acid as indicator. The concentration of H^+ was calculated by subtracting 3[Ti(III)] from the known concentration of the acid used to dissolve the Ti metal. The absence of Ti(IV) was checked spectrophotometrically in the 300-nm region.[7,8] For solutions in chloride media, Cl^- was determined by Volhard's method. The concentration of Cl^- agreed within 1% with the concentration of the acid used to dissolve the Ti metal.

Other Materials. Deionized water that had been doubly distilled through a quartz apparatus was used throughout. Baker reagent grade *p*-toluenesulfonic acid was recrystallized either from water at 80° or from water at 25° to avoid decomposition. Barium *p*-toluenesulfonate was prepared by neutralizing Baker reagent grade barium hydroxide with a 10% excess of *p*-toluenesulfonic acid in water at 60°. Cooling the concentrated solution to 0° converts the solution to a gel, but cooling to 25° yields crystalline $Ba(Tos)_2$. Trifluoromethanesulfonic acid from the 3M Co. and all other chemicals (Fisher and Baker reagent grade) were used without further purification. $LiCF_3SO_3$