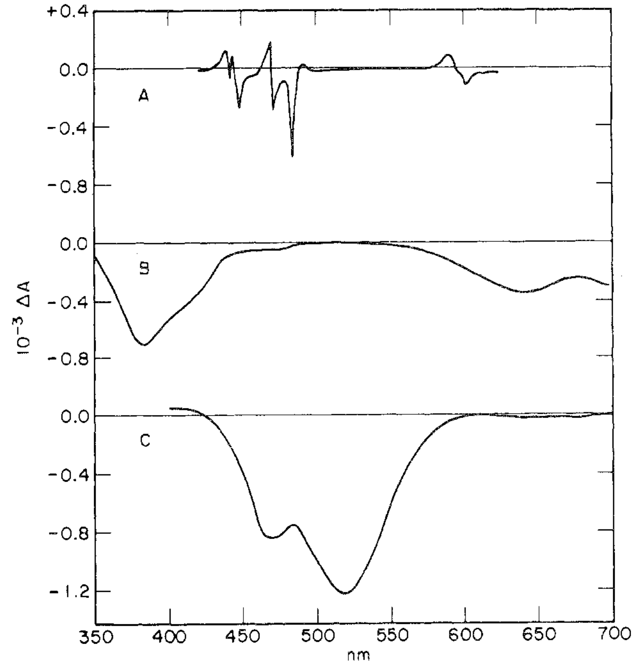

Figure 1. CD spectra of metal ion–D-(–)-quinic acid 1:1 complexes: (A) Pr^{3+} complex–upper states of transitions are $^3P_2$ (443.5 nm), $^3P_1$ (469 nm), $^3P_0$ (482 nm), and $^1D_2$ (590 nm); (B) Ni(II) complex–upper states of transitions are $\Gamma_1(^1G)$ (385 nm), $\Gamma_4(^3P)$ (408 nm), $\Gamma_5(^1D)$ (464 nm), and $\Gamma_4(^3F)$ (665 nm); (C) Co(II) complex–upper states of transitions are $^2T_{1g}$ (465 nm), $^4T_{1g}$ (517 nm), and $^4A_{2g}$ (646 nm).

hydroxyl is attached has the greater influence on the dichroism of the metal ion. With at least some metal ions, the influence of the hydroxyl ion attachment may override that of the carboxyl attachment even without deprotonation.[3]

With quinic acid, however, the spatial field at the carboxyl arises in asymmetries at the γ carbons. From the distance function implied in the dominance of the α carbon effect in the aliphatic acids, in which rotational and bending averagings along the chain are implicit in diminishing effects of more remote asymmetries, the strength of the quinic dichroism would be surprising. Presumably, then, the relative rigidity of positionings which the six-membered ring structure enforces on the carboxyl-asymmetry relation is very significant. Because of tetrahedral bonding at the 1 carbon, the carboxyl group is at an angle to the plane of the 6,1,2 carbon trio. The metal chelates, when formed between the two substituents on the 1 carbon, place the metal ion essentially *in* that plane, and presumably therefore in position to experience the maximum of the dissymmetric field. As the quantitative and qualitative effects on the metal ion transitions seem the same as those for the aliphatic α carbon asymmetric acids, the apparent lesser effects on the free carboxyl can be ascribed to geometric distribution of the field. We are left with the problem (and opportunity) of analyzing how the two different atomic situations give the same resultant asymmetric field at the α and 1 carbons.

The answer to this problem is not yet at hand. But some aid toward its answer may lie in observing that the carbonyl group of the optically active substituted cyclohexanones[7] functions as an indicator for the field asymmetry at the 1 position, parallel to the chelated metal atom of the quinic acid complexes and to the carboxyl group of the free acid (with allowance for the geometrical difference in position already cited). This comparison on spatial bases is not entirely free of questions of the influence of bonding differences. The bonds of the carbonyl carbon to the 2 and 6 carbons of the ring differ from those linking normal tetrahedral carbon at the 1 position, and even in the geometry-centered generalizations developed for the cyclohexanone systems there are definitely effects specific to the chemical nature of substituents.[8] This implies that detailed electron distribution (*i.e.*, bonding) plays a role here as it does with the metal ion chelates.

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Stoichiometric Study of the Chromium(II)-Chromium(VI) Reaction in Acidic Aqueous Chloride Media[1a]

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We are reporting a stoichiometric study of reaction 1, in acidic aqueous chloride-containing solutions, where Cr(III) includes the species $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_5Cl^{2+}$ and $Cr_2(H_2O)_8(OH)_2^{4+}$

$$3Cr(II) + Cr(VI) = 4Cr(III) \quad (1)$$

The mechanism of the reaction in aqueous chloride-free media is not yet established,[2] but it is generally thought[2-5] to include the one-electron transfers indicated in eq 2-4.

$$Cr(VI) + Cr(II) \rightarrow Cr(V) + Cr(III) \quad (2)$$

$$Cr(V) + Cr(II) \rightarrow Cr(IV) + Cr(III) \quad (3)$$

$$Cr(IV) + Cr(II) \rightarrow Cr_2(H_2O)_8(OH)_2^{4+} \quad (4)$$

Additional steps are suggested by some observations, however. Hegedus and Haim[5] observed some ^{51}Cr label in $Cr(H_2O)_6^{3+}$ product, after labeling only the Cr(VI) reactant. These authors suggest that the two-electron transfer shown in eq 5,

$${}^*Cr(V) + Cr(II) \rightarrow {}^*Cr(III) + Cr(IV) \quad (5)$$

using about 20% of the Cr(V), may account for their observation. Experiments[3,5] in which stoichiometric ratios of Cr(II) and Cr(VI) were used gave close to the 50% monomer product that is predicted by eq 2-4, or by eq 2-5. King, *et al.*,[4] working with excess Cr(VI) and low total reactant concentrations, found monomer yields ranging up to 71% of the total product. It was suggested[4] that reactions 6a and 6b may

$$Cr(IV) + H_2O \rightarrow Cr(III) + H^+ + OH \quad (6a)$$

$$Cr(II) + OH \rightarrow Cr(III) + OH^- \quad (6b)$$

account for the higher monomer yield. Additional steps that could lead to greater than 50% monomer have been proposed;[5] these are indicated by eq 7 and 8.

$$Cr(V) + Cr(IV) \rightarrow Cr(VI) + Cr(III) \quad (7)$$

$$Cr(IV) + Cr(IV) \rightarrow Cr(V) + Cr(III) \quad (8)$$

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[1] (a) Supported by the Robert A. Welch Foundation. (b) Welch Predoctoral Fellow, 1972.

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[3] M. Ardon and R. A. Plane, *J. Amer. Chem. Soc.*, 81, 3197 (1959).

[4] A. C. Adams, J. R. Crook, F. Bockhoff, and E. L. King, *J. Amer. Chem. Soc.*, 90, 5761 (1968).

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Because the details of the net electron-transfer reaction between Cr(II) and Cr(IV) are still unknown, because we are interested in Cr(V) and Cr(IV) species, and because the rate of the reaction is too great to measure by existing stopped-flow techniques,[6] we have turned to another stoichiometric study, using chloride-containing media, in an attempt to provide further details of the mechanism.

Experimental Section

Reagents. Solutions formally containing H_2CrO_4, and nearly free of potassium ion, were prepared from primary standard potassium dichromate solutions by filtering out potassium perchlorate after addition of perchloric acid. One of the solutions was analyzed spectrophotometrically[7] and was used directly in the stoichiometry experiments. Another H_2CrO_4 solution was reduced with hydrogen peroxide, and chromium(III) perchlorate was crystallized and recrystallized from water. Chromium(III) perchlorate was reduced with amalgamated zinc to obtain chromium(II) perchlorate solutions. The total chromium content of chromium(II) solutions was determined spectrophotometrically[7] after oxidation of aliquots with alkaline peroxide.

A chromium(VI) solution containing ^{51}Cr was prepared by addition of ^{51}Cr-labeled $CrCl_3$ solution (International Chemical and Nuclear Corp.) to a portion of the H_2CrO_4 solution described above; the Cr(III) was oxidized with base and hydrogen peroxide, and the peroxide was destroyed by adding platinum foil and heating in a boiling water bath for 3 hr.

Iron(II) perchlorate solutions were prepared as before.[8] Perchloric acid and hydrochloric acid solutions were prepared by dilution of the reagent grade concentrated acids and were analyzed by titration with sodium hydroxide solution. The water used in all solutions was redistilled from laboratory distilled water.

Procedures. Reactions between chromium(II) and chromium(VI) were initiated in four ways, labeled A, B, C, and D. In method A, chromium(II) was the final reagent to be added to a reaction mixture in a stirred milk dilution bottle; method B was identical with A, except chromium(VI) was added last. In method C, the stopped-flow mixing chamber[8] was used, and all the chloride was added with the chromium(II) reactant solution; method D was identical with C, except the chloride was added with the chromium(VI). Each of these procedures was carried out at room temperature in a nitrogen atmosphere. The total hydrogen ion concentration was maintained at 1.0 *M*, using HCl and $HClO_4$.

After completion of a chromium(II)–chromium(VI) reaction, an aliquot of the product mixture was passed through a column of Dowex 50W-X8 50–100 mesh ion-exchange resin in the H^+ form. The column was rinsed with dilute acid solution to remove excess chromium(VI); $Cr(H_2O)_5Cl^{2+}$ was eluted with 1.2 *M* $HClO_4$ and $Cr(H_2O)_6{}^{3+}$ was eluted with 4.0 *M* $HClO_4$; this is a standard procedure.[9] The chromium concentration of each eluted product was determined spectrophotometrically.[7] When ^{51}Cr was present, the procedure was exactly the same, except a 4.00-ml aliquot of each product solution was counted, along with a 4.00-ml aliquot of the labeled stock Cr(VI) solution. In one experiment, not listed in Table I, some ion-exchange resin attached to dimer was removed from the column, after elution of the $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_6{}^{3+}$. The dimer was oxidized with alkaline peroxide, the alkaline solution was acidified, and Ag^+ ion was added. No AgCl precipitate formed when Ag^+ was added; this test is sensitive to about 1×10^{-5} *M* Cl^-. In the sixth experiment listed in Table I, the chromium eluted with 4 *M* $HClO_4$ was neutralized to free any bound Cl^-, was reacidified, and was tested with Ag^+ ion; again, AgCl was not observed.

Reactions between chromium(II) and molecular oxygen were allowed to occur in a milk dilution bottle; the cap was removed after all the reagents had been added to the air-free bottle, and a reaction time of 20 min, with stirring, was allowed. The Cr products were separated and analyzed as described above.

Reactions between iron(II) and chromium(VI) and between copper (I) and chromium(VI) were allowed to occur and the Cr products were separated and analyzed as described above.

Results

The results of all the stoichiometry measurements are listed in Table I. These results lead to the following generalizations: (a) per cent total monomer increases as $[Cr^{2+}]_0$ decreases and as $[Cl^-]$ decreases; (b) per cent $Cr(H_2O)_5Cl^{2+}$ increases as $[Cr^{2+}]_0$ increases and as $[Cl^-]$ increases, with either Cr(VI) or molecular oxygen as the oxidant, (c) only a small amount of $Cr(H_2O)_5Cl^{2+}$ is produced when $Fe^{2+}(aq)$ or $CuCl_n{}^{(1-n)-}$ is the reducing agent, (d) 1.3% of $Cr(H_2O)_6Cl^{2+}$ formed and 4.2% of $Cr(H_2O)_6{}^{3+}$ formed apparently came from Cr(VI) in the 23rd experiment listed in Table I (note *f*); (e) the results are not affected very much by the method of mixing although the precision does not seem to be better than a few per cent, (f) the per cent of $Cr(H_2O)_5Cl^{2+}$ that is produced at very high $[Cl^-]$ is near[10] the reasonable value 25%.

Table I. Results of Stoichiometric Measurements

$[Cl^-]$, *M*	$10^3[Cr(VI)]_0$, *M*	$10^3[Cr(II)]_0$, *M*	Mixing method	% $CrCl^{2+}$ [a]	% Cr^{3+} [a]	% total monomer[a]
0	2.65	6.85	A	0.0	66	66
0	12.2	36.6	A	0.0	50	50
0.03	2.65	6.85	D	3.2	57	60
0.05	2.65	6.85	D	4.0	56	60
0.10	2.65	6.70	D	7.5	51	58
0.10	2.65	6.70	C	8.1	54	62
0.40	2.66	6.70	B	14.6	44	58
0.40	2.66	6.70	A	14.2	35	49
0.40	2.66	6.70	C	13.8	45	59
0.40	2.66	6.70	D	13.9	44	58
0.90	2.66	6.70	C	15.4	32	48
0.90	2.66	6.70	D	15.5	33	49
0.03	2.65	3.35	D	2.5	81	83
0.05	2.65	3.35	D	3.4	80	84
0.05	2.65	3.35	D	3.5	80	84
0.10	2.65	3.35	D	4.7	80	84
0.20	2.65	3.35	D	6.3	76	82
0.40	2.65	3.35	D	8.2	61	69
0.90	2.65	3.35	D	14.2	54	68
1.0	2.65	3.35	D	14.6	51	65
0.40	2.65	6.70[b]	D	0.6[c]	100	100
0.40	2.65	67.0[d]	A	9.1[c,e]	91	100
0.364	2.73[f]	6.81	B	10.7	>28	>39
0.10	[g]	9.30	A	14.6	27	42
0.40	[g]	6.70	A	7.1		
0.40	[g]	13.4	A	11.3		
0.40	[g]	26.8	A	13.6		
1.0	[g]	9.30	A	29.0	25	54

[a] The per cent is based on gram-ions of Cr that actually reacted. [b] The reducing agent was Fe(II) instead of Cr(II). [c] Note that the basis of the percentage calculation is different when Cr^{2+} is not the reducing agent; under this condition, the per cent is $100[CrCl^{2+}]/[Cr(VI) \text{ reacted}]$; when Cr^{2+} is the reducing agent, the per cent is 0.25 times this expression. The same situation exists for the % Cr^{3+} calculations. [d] The reducing agent was $CuCl_n{}^{(n-1)-}$. [e] This number probably represents an upper limit, since the sample was contaminated with copper(II). [f] Labeled with ^{51}Cr; 1.3% of the $Cr(H_2O)_5Cl^{2+}$ product came from Cr(VI) and 4.2% of the $Cr(H_2O)_6{}^{3+}$ came from Cr(VI), as determined from the labeling experiment described in the text. [g] The oxidizing agent was molecular oxygen instead of Cr(VI).

We agreed with Hegedus and Haim[5] in a repeat of one of their experiments (the second experiment listed in Table I) and with the observation by King, *et al.*,[4] that excess Cr(VI) and low total reactant concentration leads to greater than 50% monomer.

As discussed below, we think our data suggest the existence of a dimeric or polymeric chromium(II) species that contains a chloride ion. A brief spectral search provided no evidence for the dimer; a solution 0.018 *M* in Cr(II) and 1.00 *M* in Cl^- gave the same visible spectrum as a solution that was identical, but contained no Cl^-.

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(10) This value is not precise, owing to a long extrapolation from scattered data. An attempt to do an experiment in 4 *M* HCl gave additional products, including $Cr(H_2O)_4Cl_2{}^+$ and neutral or negatively charged chlorochromium species.

Discussion

Reductions of Cr(VI) have been the subjects of many mechanistic studies, and extensive evidence exists for series of one-electron transfers analogous to those shown by eq 2-4. Because of this evidence we think these steps probably do occur during net reaction 1, and in the following discussion we assume they do occur. However, our data, as those of earlier workers,[4,5] imply that additional steps occur.

Our data show that the elementary reaction(s) yielding $Cr(H_2O)_5Cl^{2+}$ and the elementary reaction(s) yielding $Cr_2(H_2O)_8(OH)_2{}^{4+}$ compete more effectively (with elementary steps yielding $Cr(H_2O)_6{}^{3+}$) at high [Cr(II)] and at high $[Cl^-]$. These observations cannot be rationalized solely by any combination of reactions 2-8.

Reactions 2-4 and various combinations of reactions 6-11

$$2Cr^{2+} + Cl^- = Cr_2Cl^{3+} \qquad Q_9 << 1 \tag{9}$$

$$Cr_2Cl^{3+} + Cr(VI) \rightarrow Cr(H_2O)_6{}^{3+} + Cr(H_2O)_5Cl^{2+} + Cr(IV) \tag{10}$$

$$Cr_2Cl^{3+} + Cr(V) \rightarrow Cr(H_2O)_5Cl^{2+} + Cr_2(H_2O)_8(OH)_2{}^{4+} \tag{11}$$

are consistent with the observations listed just above. Each of reactions 10 and 11 competes more effectively than the other reactions discussed here at high [Cr(II)] and at high $[Cl^-]$ and yields $Cr(H_2O)_5Cl^{2+}$ along with $Cr(H_2O)_8(OH)_2{}^{4+}$ or a presumed precursor of $Cr(H_2O)_8(OH)_2{}^{4+}$. Other reactions involving higher polymers of Cr(II) would also be in accord with our data. Our failure to find spectral evidence for a Cr(II) dimer indicates that (if it is indeed formed) the extent of formation is small, or the visible spectrum is similar to that of monomer.

The small amounts of $^{51}Cr(H_2O)_5Cl^{2+}$ and $^{51}Cr(H_2O)_6{}^{3+}$ produced in the labeling experiment indicate the pathways taking Cr(VI) to monomer are not major pathways under the conditions of that experiment. Yet, in the experiments at lowest $[Cr(II)]_0$ and $[Cl^-]$, greater than 75% of the product was monomer, indicating that a significant amount of Cr(VI) had to be converted to monomer. These observations are in accord with eq 10 (to produce the $Cr(H_2O)_5Cl^{2+}$) followed by eq 6a, or 7, or 8 (to produce $Cr(H_2O)_6{}^{3+}$ from Cr(VI), in greater amounts at lower Cr^{2+}) but are not in accord with eq 11. A sequence involving eq 10 as the sole process leading to $Cr(H_2O)_5Cl^{2+}$ predicts that even at very low $[Cr(II)]_0$, a labeling experiment would yield no $^{51}Cr(H_2O)_5Cl^{2+}$, but a significant amount of $^{51}Cr(H_2O)_6{}^{3+}$. We did not test this prediction by experiment, but it appears that it would have to be approximately true regardless of the mechanism, owing to the very small *total* amount of $Cr(H_2O)_5Cl^{2+}$ and the large amount of total monomer that is produced at low $[Cr(II)]_0$.

The failures to detect a large quantity of $Cr(H_2O)_5Cl^{2+}$ product when Fe(II) or Cu(I) was the reductant appear to be further evidence that Cr(VI) is not the principal source of $Cr(H_2O)_5Cl^{2+}$. This evidence and the result of the labeling experiment seem to require that $Cr(H_2O)_5Cl^{2+}$ must come primarily from the Cr(II). If Cr(II) is the source of $Cr(H_2O)_5Cl^{2+}$, then it is reasonable to expect that other oxidants could also yield $Cr(H_2O)_5Cl^{2+}$. Further, if Cr(II) *dimer* (or other polymer) is responsible for $Cr(H_2O)_5Cl^{2+}$, as we have argued, then other oxidants might also produce $Cr(H_2O)_5Cl^{2+}$ with a yield increasing with $[Cr(II)]_0$ and $[Cl^-]$. These expectations were met with molecular oxygen. In addition, oxygenation of Cr(II) has been found by other workers to be second order in Cr(II), in aqueous perchlorate media[11] and in aqueous ammonia-bromide media.[12] In both of these studies, a peroxy-bridged Cr(II) dimer was proposed. Other Cr(II) dimers that are known to exist are chromium(II) alkanoates, of which the chromium(II) acetate hydrate is the best characterized.[13]

Our attempts to gain information about the behavior of unstable Cr(IV) and Cr(V) species showed that these species do not ultimately become chlorochromium(III) species upon reduction by Cr(II) (or by Fe(II) or Cu(I)) under the conditions of our study. This result could occur because the intermediates do not form thermodynamically stable chloro complexes. If Cr(V) is an oxy anion as has been suggested,[14] then it would not be expected to form stable chloro complexes; if Cr(IV) is an aquo cation as has also been suggested,[14] then we expect it to form complexes of finite stability. The failure to convert Cr(IV) and Cr(V) to chlorochromium(III) could also arise from unfavorable rates. It is not surprising that chlorochromium(IV) complexes could form slowly relative to the lifetime of Cr(IV) or even that uncomplexed Cr(IV) could be reduced much faster than complexed Cr(IV). A more definite conclusion is that Fe(II) or Cu(I) reduction of Cr(IV) did not occur primarily by a chloride-bridged mechanism in our experiments; such reductions would have led to chlorochromium(III). It seems particularly noteworthy that even Cu(I) converted less than 10% of the Cr(VI) to $Cr(H_2O)_5Cl^{2+}$, even though Cu(I) was extensively complexed by chloride,[15] in our experiment.

The most interesting implication of this study is the unexpected one that chloride-bridged dimeric chromium(II) species exist. Our evidence indicates that this is a mechanistically significant species. We suggest that the possible existence of Cr(II) dimers should be considered in connection with other mechanistic studies, especially if complexing anions are present.

Registry No. $Cr(H_2O)_6{}^{3+}$, 14873-01-9; $Cr(H_2O)_5Cl^{2+}$, 17712-88-8; $Cr_2(H_2O)_8(OH)_2{}^{4+}$, 37380-89-5; H_2CrO_4, 7738-94-5; chromium(II) perchlorate, 13931-95-8.

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Conversion of Dihydridodiammineboron(III) Borohydride to Ammonia-Borane without Hydrogen Evolution

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It has been known for some 15 years that ammonia-borane can be formed from dihydridodiammineboron(III) borohydride.[1] In all such previous reports H_2 was observed as a product along with another product usually assumed to be $(H_2BNH_2)_n$. The equation previously written is

$$[H_2B(NH_3)_2]BH_4 \xrightarrow[\text{diethyl ether}]{NH_3} H_2 + H_3BNH_3 + (1/n)(H_2BNH_2)_n$$

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