Figure 1 the weakest lines are barely visible while in Figure 2, a high-gain presentation, all twelve lines are clearly observed.

Reaction of 2,2′-Biphenylenechloroborane with Lithium 2,2′-Bipyridine. A glass ampoule equipped with a standard break-off seal and containing 2.21 mmoles of 2,2′-biphenylenechloroborane was sealed to the side arm of a 50-ml round-bottom flask equipped with a standard break-off seal, O-ring joint, and constriction. After addition of a glass-coated stirring bar, 2.21 mmoles of 2,2′-bipyridine, and 2.2 mmoles of lithium, the apparatus was attached to the vacuum line and cooled to −78°. The apparatus then was evacuated and approximately 20 ml of tetrahydrofuran was condensed on the solids. The resulting mixture was warmed to room temperature and stirred for 10 hr. The solvent then was distilled away leaving the purple solid, lithium 2,2′-bipyridine.

After cooling the bulb to −196°, approximately 25 ml of cyclopentane was condensed in, the constriction fused, and the apparatus removed from the vacuum line. The bulb again was warmed to room temperature. Using a magnetic breaker, the break-off seal to the ampoule was opened and the sample of 2,2′-biphenylenechloroborane transferred to the bulb. The resulting mixture was shaken at room temperature for 3 days, then filtered, and the solvent removed from the filtrate by distillation at room temperature. A very sensitive brown-red residue and a white solid remained. The solid, 2,2′-bipyridine, was removed by pumping on the mixture for 48 hr at room temperature.

The brown-red, cyclopentane-soluble material was observed to decompose slowly *in vacuo* at room temperature as evidenced by the formation of a black solid. This instability made it impossible to secure a good elemental analysis, molecular weight data, and optical absorption data.

A cyclopentane solution of the freshly prepared brown-red oil was found to exhibit paramagnetism. By varying the concentration and temperature of the solution, the paramagnetic resonance was resolved into 22 lines with a total breadth of some 35 gauss.

Methanolysis of Dimethylaminoboron 2,2′-Bipyridine. An evacuated ampoule containing a sample of dimethylaminoboron 2,2′-bipyridine was attached to the vacuum line and cooled to −196° and methanol was condensed on the red material. On warming the bulb to room temperature a vigorous reaction took place as evidenced by boiling and formation of a deep blue-green paramagnetic solution

After allowing the solution to remain at room temperature for 8 hr, the color had changed to red-brown. The color change was accompanied by a decay in the paramagnetic resonance signal.

Methanolysis of Boron Bis(2,2′-bipyridine). When a sample of boron bis(2,2′-bipyridine) was treated with methanol *in vacuo*, a deep blue-green paramagnetic solution was formed having an electron spin resonance spectrum identical in hyperfine structure, but possibly slightly narrower than that of boron bis(2,2′-bipyridine).

The blue-green color changed to pale yellow in approximately 12 hr. Accompanying the color change was a decay in the paramagnetic resonance signal.

Reactions of Halogens with Tris(ethylenediamine)osmium(III) Iodide

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Abstract: The initial product of the interaction of halogens and tris(ethylenediamine)osmium(III) iodide 2-hydrate, $[Os(en)]I_3 \cdot 2H_2O$, is the trihalide. Chlorine, bromine, and iodine were used but only chlorine gave any further reaction involving the complex cation. The ICl_2^- and IBr_2^- anions gave metathesis products upon prolonged standing and the I_3^- species was stable in the solid state but decomposed slowly when dissolved in water or ethanol; the rate constant for the decomposition in ethanol was 8.70×10^{-3} min^{-1}.

Of the possible oxidation states of osmium, those in which osmium is surrounded by nitrogen-containing ligands vary from Os(VI) in $[Os(en\text{-}H)_4]I_2 \cdot 3H_2O$[1] [(en-H) = $H_2NCH_2CH_2NH^-$] to Os(0) in $[Os(NH_3)_6]$.[2] Much attention has been directed to the effect of oxidizing agents on $[Os(bipy)_3]^{n+}$ in low oxidation states[3–7] but only qualitative observations have been recorded on oxidation–reduction reactions of Os–en complexes. In view of the ease with which Os(III) is oxidized in $[Os(NH_3)_5X]X_2$ (X = Br or Cl) by bromine water or even air,[8] it was thought that the first reaction of a halogen with the tris(ethylenediamine)osmium(III) complex would be oxidation of osmium. Halogen attack on, or reaction with, the ligand might be involved if elevated temperatures were employed or acido groups were used as donor groups;[9, 10] once chlorination begins on the ligand, acido groups (chloroamido groups) would be formed.[10] Rather it was found that the first products of reaction between halogens and $[Os(en)_3]I_3 \cdot 2H_2O$ by "dry" techniques[11, 12] were the trihalides. The I_3^- and IBr_2^- compounds appeared to be the terminal products of reaction of $[Os(en)_3]I_3 \cdot 2H_2O$ with I_2 and Br_2, respectively, except for some metathesis of the IBr_2^-. The ICl_2^- compound was found to undergo further reactions involving oxidation of the central metal ion and reaction with the ligands.

Trihalides of ammine complexes are known[13] but are usually limited to triiodides. Of the trihalides, tri-

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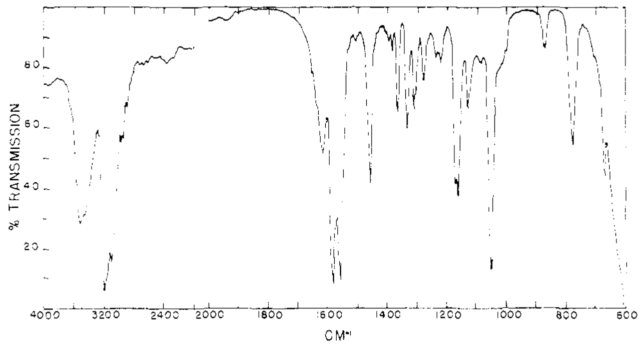

Figure 1. The infrared spectrum of $[Os(en)_3]I_3 \cdot 2H_2O$ in the 600–4000-cm^{-1} region in a KBr pellet. (A 2× ordinate expansion was used in the 600–2000-cm^{-1} region.)

iodides are usually the most stable; the dibromoiodide [or dibromoiodate(I)] and dichloroiodide [or dichloroiodate(I)] are less stable in that order with respect to dissociation in water and air (dissociation pressures).[14] The trichloride is the least stable of the trihalides characterized.[14]

Experimental Section

Magnetic susceptibility measurements were made at 25° with a Curie–Cheneveau balance and corrected for diamagnetic contributions. Infrared spectra (Table I) were obtained with a Beckman IR-7 instrument with NaCl and CsI interchanges (200 to 4000 cm^{-1}). Solid samples were observed in Nujol and high-boiling perfluorokerosene mulls and in KBr and KCl pellets. Visible and ultraviolet spectra of the compounds in both water and ethanol solutions were recorded with a Cary Model 14 spectrophotometer. X-Ray diffraction data (Table II) were obtained with Cu Kα radiation at 35 kv and 15 ma. Exposure times were ~15 hr; relative intensities were estimated visually.

Table I. Infrared Spectra in the 250–650-Cm^{-1} Region[a]

$[Os(en)_3]$-$I_3 \cdot 2H_2O$	$[Os(en)_3]$-$(I_3)_3$	$[Os(en)_3]$-$(IBr_2)_3$
560 s	555 s, u	561 s
549 s	537 w, sh	536 m
	531 m	
498 m	496 m	498 m
437 m		440 sh
425 sh	426 m	430 m
315 m, u	318 m	332 m
283 m	283 m	284 m

[a] In Nujol mulls. Symbols used: s = strong, m = medium, w = weak, sh = shoulder, u = unsymmetrical.

Analyses were performed by a micro Dumas method for nitrogen and hydrogen reduction to determine osmium. Samples of 15 to 25 mg for Os analyses were heated in a porcelain boat in a stream of H_2. The temperature was slowly brought to 460° and maintained there for 4 hr; then the sample was cooled in a stream of He and weighed as the metal. A check of the method involved heating the metal in a stream of O_2, which removed the Os as OsO_4.

Tris(ethylenediamine)osmium(III) Iodide, $[Os(en)_3]I_3 \cdot 2H_2O$. This compound was prepared as described by Dwyer and Hogarth[1] and used as starting material in other syntheses. The X-ray powder diffraction pattern and infrared spectrum for this product agreed with those recorded earlier[15] and are reported here in Table II and Figure 1, respectively.

Table II. X-Ray Diffraction Data

$[Os(en)_3]$-$I_3 \cdot 2H_2O$		$[Os(en)_3]$-$(IBr_2)_3$		$[Os(en)_3]$-$(I_3)_3$		$[Os(en)_3]$-$(ICl_2)_3$	
d, A	I/I_0	*d*, A	I/I_0	*d*, A	I/I_0	*d*, A	I/I_0
8.50	0.1[a]	5.44	0.2	4.25	0.1[a]	6.29	0.1[a]
7.16	0.9	5.13	0.3	4.13	1.0	5.88	0.3
5.20	1.0	4.46	0.1[a]	3.90	0.1	5.48	1.0
4.46	0.7	4.25	0.1	3.55	0.1	4.34	0.7
4.17	0.1	4.02	1.0	3.43	0.1	3.91	1.0
3.96	0.1	3.33	0.1	3.01	0.1	3.73	0.2
3.66	0.2	2.93	0.2	2.88	0.1	3.25	0.1
3.36	0.2	2.65	0.2	2.79	0.2	2.91	0.4
3.15	0.1	2.36	0.1	2.44	0.15	2.79	0.2
2.93	0.1	2.01	0.1	2.28	0.1	2.67	0.1
2.86	0.1	1.82	0.1	2.10	0.1	2.34	0.2
				1.89	0.1	1.96	0.1

[a] Less intense lines not included.

Anal. Calcd for $[Os(en)_3]I_3 \cdot 2H_2O$: Os, 24.16. Found: Os, 24.49.

Tris(ethylenediamine)osmium(III) Triiodide, $[Os(en)_3](I_3)_3$. A concentrated solution of I_2 in CCl_4 (5 ml) was allowed to stand over 150 mg of $[Os(en)_3]I_3 \cdot 2H_2O$ for 2 days, then filtered off and replaced by 5 ml of fresh solution. After another day the solution was filtered off, and the product was washed quickly with three 5-ml portions of CCl_4 and then dried under aspirator pressure over $Mg(ClO_4)_2$ overnight; μ_{eff} = 1.83 BM.

Anal. Calcd for $[Os(en)_3](I_3)_3$: Os, 12.57; N, 5.55. Found: Os, 12.60; N, 5.50.

The black crystalline product gave off I_2 above 190° but showed no other change up to 250°. Attempts to prepare this product by passing a stream of I_2 in N_2 over $[Os(en)_3]I_3 \cdot 2H_2O$ gave reaction that was incomplete even after several days.

Tris(ethylenediamine)osmium(III) Dibromoiodate(I), $[Os(en)_3](IBr_2)_3$. Bromine was passed over 0.4006 g of $[Os(en)_3]I_3 \cdot 2H_2O$ (0.5089 mmole) by passing dry N_2 through liquid Br_2. A gain of 0.2464 g of Br_2 (3.082 mmoles) by the solid indicates a 6.05:1 ratio of Br to complex. The product was washed with CCl_4 and dried 12 hr over $Mg(ClO_4)_2$; μ_{eff} = 1.74 BM.

Anal. Calcd for $[Os(en)_3](IBr_2)_3$: C, 5.94; H, 1.98; N, 6.93; Os, 15.60. Found: C, 6.18; H, 2.18; N, 6.88; Os, 15.82. A 24.3-mg sample gave 36.1 mg of AgX for total halogen compared with 36.7 mg calculated.

The orange-brown substance became brown on heating to 125°, gave off I_2 or IBr at >130°, and apparently decomposed above 135°.

Tris(ethylenediamine)osmium(III) Dichloroiodate(I), $[Os(en)_3](ICl_2)_3$. Chlorine gas diluted with a five- to ten-fold excess of dry N_2 was passed over $[Os(en)_3]I_3 \cdot 2H_2O$. A 0.3801-g sample of starting material gained 0.2021 g of chlorine, *i.e.*, a ratio of 0.4828 mmole to 5.693 mmoles (1:11.79) which suggests the compound $[Os(en)_3](ICl_4)_3$. However, this compound had a strong odor of Cl_2 and when washed twice with 10-ml portions of CCl_4 and dried briefly gave an analysis corresponding to $[Os(en)_3](ICl_2)_3$. An identical product was obtained by interrupting the flow of Cl_2 and N_2 and checking the weight at short intervals until a net gain of six Cl atoms/mole of starting material was attained.

Anal. Calcd for $[Os(en)_3](ICl_2)_3$: Os, 19.73; N, 8.72. Found: Os, 19.98; N, 8.68.

The product showed only traces of I_2 when leached with CCl_4 but reacted with acetone to give some I_2 and other acetone-soluble decomposition products. The $[Os(en)_3](ICl_2)_3$ was yellow-brown but became yellow upon grinding. It became brick red upon prolonged evacuation or warming; I_2 was given off above 110° and further decomposition began above 160°. At 194–196° (or upon prolonged standing in contact with air) the product became black. The magnetic moment, μ_{eff}, of the freshly prepared complex was 1.76 BM but decreased with time, thus suggesting oxidation to Os(IV).

Further reactions of Cl_2 with $[Os(en)_3]I_3 \cdot 2H_2O$ were undertaken using different conditions. Treatment of the ICl_2^- compound with acetone should have yielded[16] $[Os(en)_3]Cl_3$, but on following the reaction by checking the Os content the highest found was about 37% Os compared with 39.90% required for $[Os(en)_3]Cl_3$. Even

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repeated treatment with Cl_2 and acetone did not yield the pure chloride. The reaction was terminated in a yellow product when the acetone wash was the final treatment or in a deep brown product by treatment with Cl_2 as the last step. Treatment with concentrated Cl_2 gave a dark product which could not be restored to a yellow color by treatment with acetone. The light yellow product which was apparently an impure simple chloride became dark on prolonged exposure to air and was much less stable to heat than the iodide, changing color around 90° and decomposing below 250°.

Treatment of a CCl_4 slurry of $[Os(en)_3]I_3 \cdot 2H_2O$ with Cl_2 gave a variety of compositions ranging from about 24 to 31% osmium. Some difficulty in reproducibility was also encountered in trying to treat $[Os(en)_3]I_3 \cdot 2H_2O$ with Cl_2 beyond the stage of the ICl_2^- compound by passing Cl_2 in N_2 over the dry compound. On passing first Cl_2 (dilute) and then pure N_2 over about 150 mg of the starting material for a period of several days, black crystals of I_2 or ICl_3 and I_2 formed and were washed out with two 10-ml portions of CCl_4. By repeating this step three times, all the iodine present was apparently removed. The procedure was concluded with passage of dilute Cl_2 over the product which was dark brown and found to have an appreciable vapor pressure of Cl_2. A nitrogen analysis of 11.96% and several osmium analyses around 28% fit the composition $[Os(en)_3](Cl_3)_3$, which requires 27.6% Os and 12.17% N. However, the Os content varied with time, even in a sealed container. Chlorine was apparently lost to any atmosphere except one containing 20% or more Cl_2. The magnetic moment, μ_{eff}, was found to be 1.76 BM though some error probably resulted from loss of Cl_2. The product gave a spectrum in the ultraviolet region which was indicative of Cl_3^- in water.[17,18] The concentrated solutions gave spectra characteristic of Cl_3^- while dilute solutions did not.

Discussion

Iodine in CCl_4 or Br_2 in N_2 reacted with $[Os(en)_3]I_3 \cdot 2H_2O$ to yield the I_3^- or IBr_2^- salt of $[Os(en)_3]^{3+}$, respectively. The I_3^- compound was stable in the solid state but while checking the ultraviolet spectrum against that reported in the literature[19] for the I_3^- moiety, it was found that the spectra agreed except for some small difference in extinction coefficients and that these varied with time. Accordingly, efforts were made to measure the extinction coefficient of the species initially present, I_3^-, but owing to the time required for sample preparation this could not be done with great accuracy. By following the change in ethanol spectroscopically, however, it was possible to fit a plot of log extinction coefficient *vs.* time to a straight line, suggesting a first-order reaction. The initial spectrum agreed with that reported by Gilbert, *et al.*,[19] but also included a peak at 2180 A with log $\epsilon \sim 4.86$, and slow scanning indicated that the other maxima were at 2920 and 3575 A instead of the 2900 and 3600 A reported for CsI_3.[19] After 20 hr the apparent decomposition, $I_3^- \rightarrow I^- + I_2$ (together with possible competing reactions with the solvent), was essentially complete since the spectrum was that of I_2 in ethanol and included the I^- peak at 2180 A. The plot of log ϵ *vs.* time (in min) gave a rate constant of 8.70×10^{-3} min^{-1} for the peak at 2900 A (Figure 2). The peak at 3600 A was found to overlay the tail of the I_2 band and when correction was made for this the calculated rate constant agreed with the 2900-A peak value to within 6%. The 2180-A peak was found to vary in the opposite direction (*i.e.*, enhanced upon standing) but was present in the spectra of both I_3^- and I^-.

Ultraviolet spectra of the IBr_2^- and ICl_2^- compounds also agreed with values reported for $CsIBr_2$ and $CsICl_2$ in both water and alcohol solutions,[19] thus proving the nature of the anions. Metathesis of the IBr_2^- and ICl_2^- anions upon standing was established by observing the easily identifiable I_3^- bands in the absorption spectra of the aged products which do not appear in spectra of the freshly prepared compounds. Because of this metathesis the characterization of the compounds was performed soon after their preparation, and study of the rate of dissociation was impractical. Ultraviolet spectra of the rather transient Cl_3^- are treated in the Experimental Section.

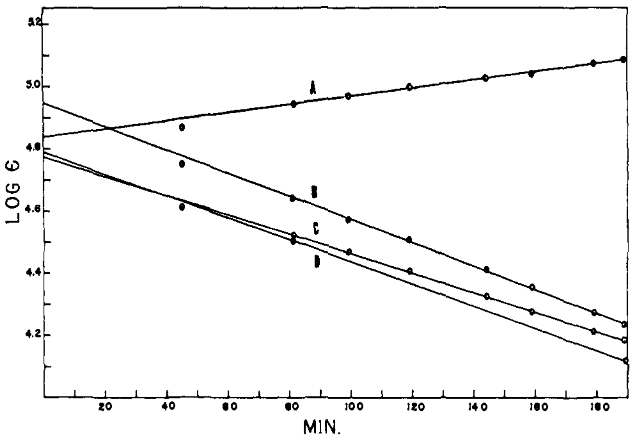

Figure 2. Variation of the ultraviolet spectrum of $[Os(en)_3](I_3)_3$ with time: A, at 2180 A; B, at 2900 A; C, at 3600 A; D, at 3600 A, corrected for the absorption by free iodine in this region. A solution 1.77×10^{-5} *M* in complex was used.

The infrared spectra of the ICl_2^-, IBr_2^-, and I_3^- compounds were found to be in agreement with the simple iodide (Figure 1) in the 600–4000-cm^{-1} region with the notable exception that the water peaks for the simple iodide were missing, and subtle differences appeared in the bands that are susceptible to hydrogen bonding.[20] The ICl_2^- compound in a KCl pellet has an infrared spectrum that is almost identical with the I^- compound in KBr except that the 775-cm^{-1} peak appears as a broad peak at 770 and a peak at 796; the 1125-cm^{-1} peak is missing. The ν_{NH} is lower, 3190 and 3085 *vs.* 3197 and 3093 cm^{-1}, and the δ_{NH} is higher, 1593 and 1570 *vs.* 1583 and 1560 cm^{-1}, in the ICl_2^- compound; this is ascribed to hydrogen bonding of both the anion[20] and the medium.[21]

The IBr_2^- compound in Nujol differed in the 1100–1200-cm^{-1} region where it included only one intense peak at 1150 and broad weak peaks at 1108 and 1200 cm^{-1}. It also showed other differences from the simple iodide in Nujol, especially the δ_{NH}.

	I^-	IBr_2^-
ν_{NH}, cm^{-1}	3182 s, 3140 (sh?), 3085 s	3200 sh, 3175 s, 3093 s
δ_{NH}, cm^{-1}	1573, 1544	1597 m, 1592 sh, 1573

The I_3^- compound in Nujol showed small shifts in the NH frequencies but differed little from the iodide in other regions: ν_{NH}, 3187 sh, 3160 s, 3075 s; and δ_{NH}, 1564 s, 1554 s cm^{-1}. Spectra of the chlorinated compounds could be obtained only in KCl since spectra in other media were obscured by background. Hence they are not included in Table I which shows differences in the 250–650-cm^{-1} region. The Cl_3^- compound was much

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like the simple iodide in the 600–4000-cm^{-1} region, except that the peaks were broad and the NH vibrations unresolved, with ν_{NH} broad and centered about 3140 while δ_{NH} was broad and centered about 1575 cm^{-1} (KCl pellet).

The stability of I_3^- is established;[14] IBr_2^- and ICl_2^- are relatively stable,[22] but Cl_3^- has been reported to be thermodynamcally unstable[23] although it was prepared[24] as early as 1923 and studied since.[14,17,18,25] It is interesting to note that the present work provided a trichloride, though not very stable, with a tripositive ion while the other known cases involve large monovalent ions, except in solution studies. Also interesting is the observation that I_2 and Br_2 react no further with $[Os(en)_3]I_3 \cdot 2H_2O$ than the reaction with the anion to form trihalides. Chlorine first forms the trihalide, and, when concentrated chlorine is used or a chlorinated compound is exposed to the air, attack on the ligand and/or oxidation of the central metal ion begins.

Acknowledgments. This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission. The initial observations on the nature of the reactions described in this paper were recorded in this laboratory by Dr. E. R. Birnbaum.

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The Reactions of Isothiocyanatobis(ethylenediamine)cobalt(III) Complexes with Chromium(II) and the Linkage Isomerization of the Monothiocyanate Complex of Chromium(III)[1]

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Abstract: The rates of reaction of chromium(II) with various *cis*- and *trans*-$Co(en)_2(NCS)X^{n+}$ complexes (where $X = H_2O$, NH_3, Cl^-, and SCN^-) have been measured at 25.0° and ionic strength 1.0 *M*. The chromium(II) attacks both the remote and the adjacent positions of the bound thiocyanate. Remote attack produces $CrSCN^{2+}$ while adjacent attack yields $CrNCS^{2+}$. The chromium(II)-catalyzed isomerization, the spontaneous isomerization, and the aquation of $CrSCN^{2+}$ were also studied. The mechanisms of these reactions are discussed.

It has long been believed that the transfer of an unsymmetrical bridging group in an inner-sphere, electron-transfer reaction would, under certain circumstances, yield an unstable product.[3,4] Intermediates produced in this manner have recently been detected. The reactions of $Co(NH_3)_5NO_2^{2+}$ and $Co(NH_3)_5CN^{2+}$ with $Co(CN)_5^{3-}$ produce the unstable species $Co(CN)_5ONO^{3-}$ and $Co(CN)_5NC^{3-}$, respectively,[5] while the reaction of $Co(NH_3)_5CN^{2+}$ with chromium(II) produces $CrNC^{2+}$.[6] We have found that the sulfur-bonded chromium(III) complex $CrSCN^{2+}$ is produced in the reaction of chromium(II) with $FeNCS^{2+}$.[7] This complex reacts with chromium(II) to form the stable nitrogen-bonded isomer $CrNCS^{2+}$

$$CrSCN^{2+} + Cr^{2+} \xrightarrow{k_c} Cr^{2+} + CrNCS^{2+} \tag{1}$$

with a rate constant of 42 M^{-1} sec^{-1} in 1 *M* perchloric acid at 25.0°. In the absence of chromium(II), $CrSCN^{2+}$ undergoes aquation and isomerization. We wish to report here that $CrSCN^{2+}$ is also produced in the reaction of chromium(II) with *cis*- and *trans*-$Co(en)_2OH_2(NCS)^{2+}$ and to describe some additional properties of $CrSCN^{2+}$.

Experimental Section

Materials. Iron(III) perchlorate was purified by recrystallization from perchloric acid. A stock solution approximately 0.5 *M* in iron(III) and 1.5 *M* in perchloric acid was prepared from the recrystallized iron(III) perchlorate. The concentration of the iron(III) in the stock solution was determined by reduction of the iron(III) with a Jones reductor and titration of the iron(II) produced with standard cerium(IV) sulfate using ferroin as indicator. The perchloric acid concentration of the stock solution was determined by precipitating iron(III) hydroxide with excess standard alkali and back-titrating with standard acid to a phenolphthalein end point.

Stock solutions approximately 10^{-1} and 10^{-2} *M* in chromium(II) and 1 *M* in perchloric acid were prepared by the reduction of chromium(III) perchlorate solutions with amalgamated zinc. The chromium(II) concentration was determined by titration with a standard iron(III) solution containing a two- to threefold excess of thiocyanate. The disappearance of the red iron(III) thiocyanate complexes was taken as the end point. The perchloric acid concentration of the chromium(II) solution was determined by oxidiz-

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

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