

where AP is the appearance potential (14.5 eV) of the $\text{CH}_3\text{SiF}_2^+$ ion cited in Table I. The ionization potential of CH_3SiF_2 thus calculated is 265 kcal/mol or 11.5 eV.

It would be desirable to compare the values reported here with values determined by other methods. Unfortunately, there is no literature available for such a comparison. However, $I(\text{CH}_3\text{SiF}_2)$ can be independently estimated and since $I(\text{CH}_3\text{SiF}_2)$ reported above depends on the values reported for the other quantities, such a comparison can serve as a check on the $\text{CH}_3\text{SiF}_2\text{-Co}(\text{CO})_4$ bond energy and on the estimation of $\Delta H_f^\circ(\text{CH}_3\text{SiF}_2)$.

The ionization potential of $(\text{CH}_3)_3\text{Si}$ is 6.94 eV¹⁵ and the ionization potential of F_3Si is 13.3 eV.¹⁶ Thus, the ionization potential is reduced an average of 2.12 eV for every fluorine atom replaced by a methyl group and the ionization potential of CH_3SiF_2 is estimated to be 11.18 eV. This value is in reasonable agreement with the value of 11.5 eV reported for $I(\text{CH}_3\text{SiF}_2)$ above. While this substituent effect extrapolation may be somewhat tenuous, it appears legitimate in view of the paucity of data available for this type of compound. This agreement is gratifying and furnishes some support of the values reported for $\Delta H_f^\circ(\text{CH}_3\text{SiF}_2)$ and $D(\text{CH}_3\text{SiF}_2\text{-Co}(\text{CO})_4)$. However, as stated previously, there is no assurance that the measured appearance potentials did not contain excess energy or that $\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4$ did not thermally decompose in the ion source, and the data reported must be considered in light of these possible errors. Nevertheless, until the thermodynamic values of $\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4$ can be measured by another method, e.g., calorimetry, the values cited here are the best acceptable estimates now available.

(15) G. G. Hess, F. W. Lampe, and A. C. Yergey, *Ann. N. Y. Acad. Sci.*, **136**, 106 (1966).

(16) J. D. McDonald, C. H. Williams, J. C. Thompson, and J. L. Margrave, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract O-173.

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Stoichiometry and Kinetics of the Reduction of the Chloroerythrochromium(III) Ion by Chromium(II)

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The binuclear chromium(III) complex $(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{Cl}^{4+}$, commonly known as the chloroerythro ion, contains two chemically different chromium atoms, either of which, in principle, could accept an electron from a one-electron reducing agent. If a one-electron reduction occurred *via* a bridged activated complex, attack by the reducing agent would be expected to

occur at the chloride ion, which is an effective bridging group, so that the incoming electron would reach the tetraammine chromium first. It should be noted, however, that the two chromium atoms of the complex are connected by means of a hydroxo bridge, and the hydroxide ion is at least as effective an electron mediator as is the chloride ion.¹ Thus the introduction of an electron onto the tetraammine chromium atom would generate a moiety having some the characteristics of an inner-sphere activated complex for electron transfer, namely, two metal centers capable of exchanging an electron and linked by a bridging group. It might then be possible for an electron to pass through the chromium atom of the tetraammine fragment and reduce the chromium atom of the pentaammine fragment.

The one-electron reducing agent which we have chosen to treat with the chloroerythro ion is the aquochromium(II) ion, the reaction being the chromium(II)-catalyzed loss of ammonia from the binuclear complex in acidic aqueous solutions.

Experimental Section

Chloroerythrochromium(III) chloride, $[\text{Cr}(\text{NH}_3)_5(\text{OH})\text{Cr}(\text{NH}_3)_4\text{Cl}]\text{Cl}_4$, was prepared according to the method of Linhard and Weigel.² The perchlorate salt of the dimer, $[\text{Cr}(\text{NH}_3)_5(\text{OH})\text{Cr}(\text{NH}_3)_4\text{Cl}](\text{ClO}_4)_4$, was prepared by stirring the solid chloride salt together with slightly less than the stoichiometric amount of solid AgClO_4 in dilute HClO_4 , filtering the solution to remove AgCl , and precipitating the complex from the cold filtrate with 70% HClO_4 . The perchlorate salt was recrystallized several times from dilute perchloric acid. Since the solid perchlorate salt decomposes rather quickly, it was prepared on the same day it was to be used. *Anal.* Calcd for $[(\text{NH}_3)_5\text{Cr}_2(\text{OH})\text{Cl}](\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$: N, 16.55; Cr, 13.65. Found: N, 16.39; Cr, 13.51 (N/Cr = 4.50).

Chromium(II) perchlorate solutions were prepared by the dissolution of weighed samples of 99.99% pure chromium metal (United Mineral and Chemical Corp.) in 1 M HClO_4 . The chromium(II) solutions were prepared, stored, and otherwise handled under an atmosphere of nitrogen gas, which had been freed of oxygen by passage through chromium(II) perchlorate solutions. The chromium(II) solution was dispensed by means of a microburet connected to the storage flask and fitted with a hypodermic needle. The chromium(II) content of the solution was determined by reaction with excess standard iodate solution followed by back-titration of the iodate (as I_2) with standard sodium thiosulfate.³ Total chromium was determined volumetrically⁴ as dichromate after oxidation with alkaline peroxide.

The reaction vessel for kinetic measurements was a quartz spectrophotometric cell onto which a small side compartment had been sealed. A solution containing the desired amounts of the chloroerythro perchlorate, sodium perchlorate, and perchloric acid was placed in the main part of the cell, and both compartments of the cell were sealed with rubber serum caps. The cell was deaerated with a stream of prepurified nitrogen and filled with nitrogen at about 5 psi above atmospheric pressure; then the desired amount of chromium(II) perchlorate solution was injected into the side compartment. The contents of the cell were brought to a chosen temperature by immersion of the cell in a water bath. The cell was inverted, shaken vigorously to mix the contents, and placed immediately in the thermostated cell compartment ($\pm 0.1^\circ$) of a Cary Model 15 spectrophotometer. The recording of absorbance *vs.* time was begun less than

(1) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(2) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **299**, 15 (1959).

(3) H. W. Stone, *Anal. Chem.*, **20**, 747 (1948).

(4) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, Longmans, Green and Co., Ltd., London, 1961, p 311.

10 sec after the beginning of mixing. This same procedure was used to prepare the solutions whose spectra were recorded as a function of time as a means of establishing reaction stoichiometry.

The progress of the reaction was followed at 500 m μ . Since chromium(II) is not consumed in the reaction under study, pseudo-first-order rate constants, k_{obsd} , were obtained from the slopes of plots of $\log(A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbances at time t and at the end of the reaction, respectively. Since the reaction of the chloroerythro ion with chromium(II) is followed by a much slower reaction of the products (see Results and Discussion), a completely steady A_∞ was never reached, and A_∞ was taken to be the absorbance after *ca.* 7 half-lives.

To establish reaction stoichiometry, the reaction was quenched at various stages by the oxidation of chromium(II) with atmospheric oxygen. The reaction products were separated on a column of Dowex 50W-X2 or 50W-X8 cation-exchange resin and eluted with perchloric acid. The species present in the various fractions from the column were identified by their absorption spectra. The chromium content of each fraction was determined volumetrically.⁴ Fractions were tested for free chloride with silver nitrate. Bound chloride was determined by first destroying the complex ion by base hydrolysis and then titrating the acidified solution potentiometrically against standard silver nitrate. Chromium and chloride analyses were performed using separate aliquots to avoid interference from chromate in the chloride analysis, and the Cl/Cr ratios were determined.

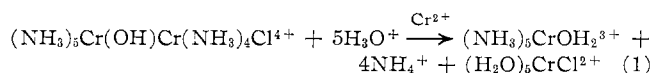
Results and Discussion

It was expected that the one-electron reduction of the chloroerythro ion would yield a monomeric chromium(III)-ammine complex as one product and that this product would be subject also to chromium(II)-catalyzed loss of ammonia. In agreement with this expectation, it was observed that the addition of chromium(II) to acidic solutions of the chloroerythro ion gave an initial rapid change in the spectrum followed by a much slower change. For example, at 435 m μ the absorbance increased rapidly and then decreased very slowly following the addition of chromium(II). When the chromium(II) concentration was made sufficiently large to give a convenient rate for the second reaction, the first reaction became immeasurably fast. It seemed likely that the rapid reaction was the reaction of the chloroerythro ion and that the slower reaction was that of a monomeric product with chromium(II). Consequently, the stoichiometry of the first reaction was investigated by separating and identifying the species present in reaction mixtures quenched during or immediately after the rapid reaction.

Five chromium-containing species were found in the reaction mixtures quenched prior to the completion of the rapid reaction. No free chloride was detected in any of the fractions from the ion-exchange columns. The complex cation eluted most readily from the cation-exchange column (with 1 *M* HClO₄) had a Cl/Cr atom ratio of 0.98 ± 0.05 , and was identified by its spectrum as (H₂O)₅CrCl²⁺. The second fraction to be eluted (with 1.5 *M* HClO₄) was Cr(H₂O)₆³⁺ and was present in an amount approximately equal to that introduced with the chromium(II) solution. The third fraction eluted (with 2 *M* HClO₄) was identified as (NH₃)₅-CrOH₂³⁺ by its spectrum. The other possible aquoammine species, *cis*- and *trans*-(NH₃)₄Cr(OH₂)₂³⁺, have

absorption spectra⁵ sufficiently different from that of (NH₃)₅CrOH₂³⁺ that there is no doubt that the pentaammine rather than a tetraammine complex is the product of the reaction. Further, the diaquotetraammine complexes are separated from the aquopentaammine ion on Dowex 50W-X2 resin by procedures used here.⁵ In some cases it was possible to precipitate [(NH₃)₅Cr(OH₂)](ClO₄)₃ from the eluent fractions. The fourth fraction, eluted with 2.5 *M* HClO₄, was identified as the binuclear series (H₂O)₄Cr(OH)₂Cr(H₂O)₄⁴⁺ and was found in approximately the amount expected from the oxidation of chromium(II) by atmospheric oxygen.⁶ After the removal of the latter species, a faint pink band, identified as unreacted chloroerythro ion from its strong adherence to the resin, remained at the top of the column.

In a typical stoichiometry experiment in which 0.303 mmol of the chloroerythro ion was allowed to react with Cr²⁺ for *ca.* 6 half-times in 1.0 *M* HClO₄, 0.300 mmol each of (NH₃)₅CrOH₂³⁺ and of (H₂O)₅CrCl²⁺ were obtained by ion-exchange separation of the reaction mixture. In a number of other experiments of this type the amounts of (NH₃)₅CrOH₂³⁺ and (H₂O)₅CrCl²⁺ found never differed by more than 5% and accounted almost quantitatively for the amount of chloroerythro ion which disappeared in the reaction. It may then be concluded that the reaction of chromium(II) with the chloroerythro ion obeys the stoichiometry



Kinetic data for the chromium(II)-catalyzed aquation reaction (presented in Table I) are consistent with a rate law of the form: rate = $k[\text{Cr}^{2+}][\text{Cr}_2(\text{NH}_3)_9(\text{OH})\text{Cl}^{4+}]$. The Arrhenius activation energy, calculated from the data of Table I, is 9.2 kcal/mol.

TABLE I
SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF THE
CHLOROERYTHRO ION WITH CHROMIUM(II) IN 1 *M* HClO₄

Temp, °C	10 ³ [Cr ²⁺], <i>M</i>	$k,^a M^{-1} \text{sec}^{-1}$
15.0	3.03	1.74
	3.72	1.74
	4.38	1.80
	5.64	1.64
	6.82	1.80
20.0	3.03	2.28
	5.64	2.18
25.0	3.03	2.96
	4.38	3.08
	5.64	2.96

^a $k = k_{\text{obsd}}/[\text{Cr}^{2+}]$; k_{obsd} is the first-order rate constant.

The form of the rate law and the occurrence of Cr(H₂O)₅Cl²⁺ as a reaction product suggest that the rate-determining step of the chromium(II)-catalyzed reaction is an electron-transfer reaction in which the chloride ion serves as a bridging ligand, as anticipated in the introduction.

Since formation of tetraammine products is not

(5) D. W. Hoppenjans and J. B. Hunt, submitted for publication.

(6) R. Kolaczowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).

indicated by the stoichiometric data, it appears that the electron which enters the chloroerythro ion in the redox step never reaches the pentaammine chromium, although the pentaammine chromium(III) must be connected by means of a hydroxo bridge to a chromium(II), *i.e.*, to the reduced tetraammine fragment, for *ca.* 10^{-9} sec, the lifetime of a ligand in the first coordination sphere of chromium(II).⁷ A possible interpretation of these results is that the existence of a bridged complex is not sufficient to ensure electron transfer between the two metal ions involved.⁸ It is also possible, however, that the reduction of the pentaammine fragment is thermodynamically less favorable than reduction of the tetraammine fragment.

It is interesting to compare the reaction of the chloroerythro ion with chromium(II) to reactions of some similar chromium(III) complexes with Cr(II) also. There is very good evidence⁹ that the chloroerythro ion has the *trans* configuration, *i.e.*, that the chloride ligand is located *trans* to the bridging oxygen atom. The chloroerythro ion is then formally a derivative of the *trans*-Cr(NH₃)₄(OH₂)Cl²⁺ ion, derived by the replacement of an H atom on the water molecule of the chloroaquo complex by the Cr(NH₃)₅ fragment. At 25° and in 1 M HClO₄, the second-order rate constant for the reaction of the chloroerythro ion with Cr²⁺ is 3.0 M⁻¹ sec⁻¹, whereas *k* for the reaction of the *trans*-chloroaquo complex with Cr²⁺ is only 1.1 M⁻¹ sec⁻¹ under the same conditions.¹⁰ Thus the binuclear complex reacts more rapidly with Cr²⁺ than does the mononuclear complex, although the activated complex bears a charge of +6 in the case of the binuclear complex and only +4 for the mononuclear ion. It has been shown recently¹⁰ that the Cr-O bond of *trans*-Cr(NH₃)₄(OH₂)Cl²⁺ must be stretched substantially in forming the activated complex for reaction with Cr²⁺. It may be that the character of the Cr-O bond is changed sufficiently by the substitution of the Cr(NH₃)₅ fragment for an H atom to account for the increased rate of reaction.

Acknowledgment.—The authors are grateful to the National Science Foundation for the financial support through Grant GP-5425 and to the National Aeronautics and Space Agency for fellowship support for D. W. H.

(7) C. W. Meredith, Thesis; Lawrence Radiation Laboratory Report UCRL-11704, University of California, Berkeley, Calif., 1965.

(8) A considerable energy mismatch between the pentaammine and tetraammine fragment probably is produced during the formation of the activated complex for the transfer of the electron to the tetraammine fragment. However, this mismatch is probably not as great as that between ground-state chromium(II) and chromium(III) ions. In attempting to answer why the electron does not reach the pentaammine fragment, it should be noted that analogous binuclear chromium(III) complexes have magnetic moments only slightly lower than predicted by the spin-only formula (A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961)), indicating little electronic interaction between the metal ions. However, the electrons responsible for the paramagnetism are located primarily in T_{2g} orbitals, whereas the electron transfer is presumably between E_g orbitals.

(9) For example, acid cleavage of the chloroerythro ion yields *trans*-Cr(NH₃)₄(OH₂)Cl²⁺ as the almost exclusive tetraammine product.

(10) Sr. M. J. DeChant and J. B. Hunt, *J. Am. Chem. Soc.*, **89**, 5988 (1967).

Polycyclic Group V Ligands. IV. 2,6,7-Trithia-4-methyl-1-phosphabicyclo- [2.2.2]octane and Derivatives

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Bicyclic phosphorus compounds of the type P(YZ)₃-CCH₃, where YZ = OCH₂,² CH₂O,³ and N(CH₃)CH₂,⁴ and some of their ligand properties have been reported in previous communications from our laboratories. In order to facilitate our study of phosphorus ligands having approximately constant steric requirements while varying the electronegativity of the YZ group, the compound P(SCH₂)₃CCH₃ (I) and its 1-sulfo (II) and 1-oxo (III) derivatives, as well as the arsenic analog of I (IV), are described. The measurement of the dipole moments of I, of IV, and of the oxa analogs P(OCH₂)₃CCH₃ and As(OCH₂)₃CCH₃ allow for the first time a calculation of an approximate value for the P-S, P-O, As-S, and As-O bond moments from structural considerations. The infrared and H¹ nmr spectral properties of I-IV are contrasted with those of their trioxa analogs.

Experimental Section

A Varian A-60 spectrometer was used to obtain the H¹ nmr spectra. Molecular weights were determined by observing the position of the ion of highest mass on an Atlas CH4 single-focusing mass spectrometer at 70 eV. Infrared spectra were measured in KBr pellets on a Perkin-Elmer Model 21 spectrophotometer. Analyses were carried out by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Dipole moments were measured with a heterodyne-beat apparatus described elsewhere.⁵ Melting points are uncorrected.

Starting Materials.—The trimercaptan (HSCH₂)₃CCH₃ was prepared as described elsewhere⁶ with the modification that, at the end of the distillation of the benzene-water azeotrope, enough dry tetrahydrofuran was added to make a slush of the product after the benzene was completely removed. The sodium-liquid ammonia reduction was then carried out on this slush which permitted good mixing rather than on the hard mass that resulted otherwise. Tris(dimethylamino)phosphine was prepared as previously described⁷ and the arsenic analog was synthesized in 45% yield in a similar manner.

P(SCH₂)₃CCH₃ (I).—To 3.00 g (17.9 mmol) of the trimercaptan stirred at 70° under nitrogen was added dropwise over a period of 15 min 3.00 g (18.4 mmol) of P(N(CH₃)₂)₃. After the evolution of dimethylamine subsided, the temperature was raised to 160° and held there for 30 min. The solid which formed on cooling was treated with 5 ml of benzene and filtered. The white solid

(1) Alfred P. Sloan Fellow.

(2) K. J. Coskran, T. J. Huttemann, and J. G. Verkade in *Advances in Chemistry Series*, No. 62, American Chemical Society, Washington, D. C., 1966, p 590.

(3) E. J. Boros, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, **7**, 165 (1968).

(4) Part III: B. L. Laube, R. D. Bertrand, G. A. Casedy, R. D. Compton, and J. G. Verkade, *ibid.*, **6**, 173 (1967).

(5) A. C. Vandembroucke, R. W. King, and J. G. Verkade, *Rev. Sci. Instr.*, **39**, 558 (1968).

(6) W. von E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, **77**, 509 (1955).

(7) A. Burg and P. J. Slota, *ibid.*, **80**, 1107 (1958).