and leaving the d_{z^2} orbital vacant. By this procedure, each nickel "receives" 16 electrons.

Within the metal atom cluster, the vacant p_z orbital (A) of Ni^A and the d_{z^2} orbitals (A + E*) of the three Ni^B atoms interact to produce three bonding MO's, which are filled by the six π electrons from the three carbon–carbon double bonds (A + E) of the C_4F_6 groups, which are directed through the middle of the three faces. The metal cluster as a whole has two electrons less than the krypton configuration.

Thus the bonding in $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$ is unusual in that the π bonds from the $\pi\text{-}(CF_3)_2C_2$ ligands are directed not just to one metal atom as is customary, but to a delocalized system of four metal atoms. It is well established that CO groups can bridge three metal atoms as in $[\pi\text{-}C_5H_5Ni]_3(CO)_2$[16] and $Rh_6(CO)_{16}$[17] and recently it has been established[18] that the diphenylacetylene groups in the violet isomer of $(C_6H_5C\equiv CC_6H_5)_2Fe_3(CO)_8$ are located on opposite sides of a triangle of iron atoms. Species with structural features similar to those proposed for $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$ may be intermediates in the metal carbonyl catalyzed trimerization of acetylenes.[19]

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Kinetics and Mechanism of the Reaction of Chloropentaamminechromium(III) Ion and Mercury(II)[1a]

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The mechanisms of relatively few reactions of halochromium(III) complexes with mercury(II) ion have been reported. The aquation of $Cr(NH_3)_5Cl^{2+}$ appeared quite interesting, for the analogous reactions of $Cr(OH_2)_5Cl^{2+}$ have been studied.[2] Mercury(II) efficiently accelerates release of chloride ion from the primary coordination sphere of chromium(III). The reactions taking place are

$$Cr(NH_3)_5Cl^{2+} + Hg^{2+} + H_2O = Cr(NH_3)_5(OH_2)^{3+} + HgCl^+ \quad (1)$$

$$Cr(NH_3)_5Cl^{2+} + HgCl^+ + H_2O = Cr(NH_3)_5(OH_2)^{3+} + HgCl_2 \quad (2)$$

We have carried out studies on the kinetics and mechanisms of these reactions. Special attention was directed toward the hydrogen ion dependence of the rate and toward a comparison of the rate at which release of chloride ion is increased by mercury(II) relative to spontaneous aquation. A comparison is made of the kinetic effect of those ligands on chromium(III), NH_3 and H_2O, which remain unchanged.

Experimental Section

The compound $[Cr(NH_3)_5Cl]Cl_2$ was prepared according to the method of Schlessinger.[3] The perchlorate salt was precipitated from solutions of the chloride by slow addition of a solution of lithium perchlorate or perchloric acid and cooling. The precipitate was washed with ice-cold water, ethanol, and ether and was dried in air. Both the chloride and perchlorate salts were stored in opaque containers to prevent photochemical decomposition which otherwise occurs. The compound $[Cr(NH_3)_5OH_2](ClO_4)_3$ was prepared from the chloro complex by the method of Linhard and Berthold.[4] The visible and ultraviolet absorption spectra of these complexes agree with published data.[5,6] Other reagents were prepared and analyzed as described previously. The spectrophotometric rate measurements generally were made at 3760 A on solutions in thermostated 10-cm silica cells; the procedure was similar to that previously employed.[2]

The initial concentration of mercury(II) was always at least 20 times that of $Cr(NH_3)_5Cl^{2+}$, and the reaction followed pseudo-first-order kinetics in every experiment. Rate constants were evaluated graphically, usually taking data to at least 90% completion, and generally were reproducible to within 2–5% average deviation. Spectral measurements on spent reaction solutions proved that the reaction product is $Cr(NH_3)_5OH_2^{3+}$ as written in eq 1 and 2.

The effects of ionic strength and anion concentration on similar reactions at relatively high reactant concentrations have been considered in the earlier study of the related $Cr(OH_2)_5Cl^{2+}$–Hg^{2+} reaction.[2] As a consequence of these results, our rate measurements on both Hg^{2+} and $HgCl^+$ were carried out in an ionic medium which preserves both constant ionic strength and constant perchlorate ion concentration. All the data reported here refer to a medium of ionic strength 2.00 M, consisting of 0.50 M divalent ions (Ba^{2+}, Hg^{2+}, $Cr(NH_3)_5Cl^{2+}$) and 0.50 M univalent ions (H^+, Li^+, $HgCl^+$); perchlorate ion remained constant at 1.50 M. Appropriate changes in $[Ba^{2+}]$ or $[Li^+]$, presumed to exert no specific effects other than electrolyte effects, compensated for changes in concentration of any other substance.

Results

The rate data obey the equation

$$-d[Cr(NH_3)_5Cl^{2+}]/dt = [Cr(NH_3)_5Cl^{2+}](k_0[Hg^{2+}] + k_1[HgCl^+]) \quad (3)$$

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(1) (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1824; (b) Undergraduate research participant, summer 1965.

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(6) Our values for absorption maxima, A (molar absorbance index, M^{-1} cm^{-1}), for $Cr(NH_3)_5Cl^{2+}$ are 3760 (37.3) and 5120 (36.9). These values can be compared to 3750 (39) and 5120 (36),[5a] 3760 (43.6) and 5140 (38.0),[5b] 3750 (34.7) and 5120 (33.9),[5c] 3750 (31.7) and 5080 (40).[5d]

TABLE I

DETERMINATION OF THE ORDER OF THE Hg^{2+}–$Cr(NH_3)_5Cl^{2+}$ REACTION[a]

$[Hg^{2+}]$, M[b]	Values of k_0 ($= -[Hg^{2+}]^{-1}$ d ln $[Cr(NH_3)_5Cl^{2+}]/dt$, M^{-1} sec^{-1}) at various temperatures: 15.0°	25.0°	35.0°	45.0°
0.0500		0.0787, 0.0801	0.185, 0.190	0.456, 0.440
0.100		0.0825, 0.0856	0.198, 0.202	0.481, 0.499
0.150	0.0345, 0.0350	0.0812, 0.0834	0.199, 0.208	0.440, 0.513
0.200		0.0889, 0.0912	0.187, 0.197	
0.250	0.0351, 0.0358	0.0890, 0.0895	0.237, 0.237	
0.300		0.0905, 0.0928		
0.350	0.0381, 0.0388	0.0879, 0.0928		
0.400		0.0937		
0.500		0.0867, 0.0867		
Av k_0[c]	0.0361 ± 0.0016	0.0871 ± 0.0045	0.214 ± 0.020	0.468 ± 0.031
Calcd k_0[d]	0.0353	0.0873	0.204	0.453

[a] $[Cr(NH_3)_5Cl^{2+}]_0 \sim 2.5 \times 10^{-3}$ M in most experiments. [b] $Ba(ClO_4)_2$ added such that the total concentration of divalent cations was 0.50 M; also 0.50 F $HClO_4$. [c] Standard deviation given. [d] From the activation parameters presented in the text.

TABLE II

PSEUDO-FIRST-ORDER RATE DATA FOR THE $HgCl^+$–$Cr(NH_3)_5Cl^{2+}$ REACTION

[Hg(II)], F	$[Cl^-]$, F	$t_{1/2}$, sec: 15.0°	25.0°	35.0°	45.0°
0.200	0.300	210, 231	91	39.0, 41.5	15.4, 16.2
0.250	0.300	116, 120	49.5, 50.0	22.5, 23.0	10.4
0.250	0.400	197, 216	82, 88	49.5, 50.0	14.9, 15.0
0.300	0.500	...	...	47	17.5

In experiments on the effect of Hg^{2+}, this species alone was present at significant concentration. In evaluation of the rate constant for $HgCl^+$, the k_0 term could not be suppressed entirely, however, and its calculated contribution was subtracted from the total.

Table I summarizes the results on the Hg^{2+} reaction of a series of kinetic experiments used to establish the reaction orders. The value of the second-order rate constant is independent of hydrogen ion concentration. In a series of experiments covering the range 0.05–0.50 M H^+ at 0.50 M Hg^{2+}, the value of k_0 was constant to within an average deviation of 3.0% at 15.0°, 2.5% at 25.0°, and 4.5% at 35.0° (studied 0.10–0.50 M H^+ only); the variation was random, and no trends in k_0 with $[H^+]$ were apparent in these data.

TABLE III

RATE CONSTANTS k_1 (M^{-1} SEC^{-1}) FOR THE $HgCl^+$–$Cr(NH_3)_5Cl^{2+}$ REACTION BASED ON DIFFERENT VALUES OF Q_4

Composition		15.0°		25.0°		35.0°		45.0°	
[Hg(II)], F	$[Cl^-]$, F	$Q_4 = 0.25$	$Q_4 = 1.0$	$Q_4 = 0.25$	$Q_4 = 1.0$	$Q_4 = 0.25$	$Q_4 = 1.0$	$Q_4 = 0.25$	$Q_4 = 1.0$
0.200	0.300	0.036	0.044	0.087	0.104	0.195	0.229	0.51	0.61
0.250	0.300	0.037	0.046	0.086	0.108	0.178	0.220	0.40	0.48
0.250	0.400	0.038	0.044	0.090	0.108	0.188	0.216	0.52	0.63
0.300	0.500	...	...	...	...	0.15	0.17	0.43	0.49

Interpretation of the kinetic data on the $HgCl^+$ reaction is not without ambiguity since position of the equilibrium

$$2HgCl^+ = HgCl_2 + Hg^{2+} \qquad (4)$$

is uncertain. Appreciable concentrations of Hg^{2+} were present in solutions used in studying the reaction of $HgCl^+$. Various workers have studied the mercury(II) chloride equilibria;[7,8] Pechanski[8] determined the value $Q_4 = [HgCl_2][Hg^{2+}][HgCl^+]^{2-} = 0.40$ at 17.0° and 1.00 M ionic strength ($NaClO_4$).

We have tried several values of Q in the range 0.25–1.0, and the fit is not appreciably better for any of these. The experimental results are summarized in Table II, and the derived rate constants, using the extreme values of Q, 0.25 and 1.0, are given in Table III. The value of k_1 in each experiment was computed from the relation

$$k_1 = (0.693/t_{1/2} - k_0[Hg^{2+}])/[HgCl^+] \qquad (5)$$

with concentrations of the mercury species calculated from the formal concentrations using each particular value of Q_4 and with the value of k_0 determined previously. These computations demonstrate that these results are not very sensitive to the value of Q_4 chosen and that constancy of the values of k_1 calculated for different solutions cannot be used as an effective criterion for selecting a value of Q_4.

The interpretation of the data on the $HgCl^+$ reaction assumes $HgCl_2$ does not possess significant catalytic effects toward $Cr(NH_3)_5Cl^{2+}$. With 0.10 F $HgCl_2$ (also 0.50 F $Ba(ClO_4)_2$ and 0.50 F $HClO_4$), the pseudo-first-order rate constant for aquation of $Cr(NH_3)_5Cl^{2+}$ is $\sim 1.3 \times 10^{-4}$ sec^{-1} at 35°, compared to 0.3×10^{-4} sec^{-1} for the spontaneous aquation in 1.0 F $HClO_4$ at this temperature.[5a,9] Contributing also to the observed rate is $\sim 1.7 \times 10^{-4}$ M $HgCl^+$ present in 0.10 F $HgCl_2$,[7] which provides 0.4×10^{-4} sec^{-1}. An upper limit on the second-order rate constant for $HgCl_2$ is then 0.6×10^{-4} sec^{-1}/0.1 M = 6×10^{-4} M^{-1} sec^{-1} at 35°. The $HgCl_2$ present in the solutions used to study the

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$HgCl^+$ reaction does not contribute significantly to the aquation rate.

The temperature dependences of the rate constants k_0 and k_1 were described in terms of the activation parameters ΔH^* and ΔS^* in the absolute rate theory equation, $k = (k_BT/h)e^{-\Delta H^*/RT}e^{\Delta S^*/R}$. The values of k_0 and k_1 listed in Tables I and III were fit to this equation with a nonlinear least-squares program[10] with the following results. For Hg^{2+}, $\Delta H^* = 14.9 \pm 0.2$ kcal mole^{-1} and $\Delta S^* = -13.4 \pm 0.7$ cal mole^{-1} deg^{-1} with the indicated uncertainties representing standard deviations. In the case of $HgCl^+$, the calculation used values of k_1 based on different estimates for Q_4 in the range 0.25–1.0. The activation parameters are not especially sensitive to the choice of Q_4; for the values 0.25, 0.38, and 1.0, ΔH^* is 14.3 ± 0.6, 14.4 ± 0.5, and 14.1 ± 0.6 kcal mole^{-1}, respectively. The corresponding values of ΔS^* all lie within 2 eu of -15 eu.

Discussion

The observed lack of dependence of the rate of reaction 1 on hydrogen ion appears significant, especially in view of the importance, in the analogous reaction of $Cr(OH_2)_5Cl^{2+}$, of a rate law term k_{-1} $[Cr(OH_2)_5Cl^{2+}]\cdot[Hg^{2+}]/[H^+]$ in a region of $[H^+]$ where no appreciable acid ionization of the reactants takes place.[2] Two mechanisms which are consistent with the kinetics for this pathway both involve a very slight extent of an acid dissociation of one reactant, followed by the rate-determining bimolecular reaction of its basic form with the second reactant. The question of whether this path corresponds to reaction of $Cr(OH_2)_4(OH)Cl^+$ and Hg^{2+} or of $Cr(OH_2)_5Cl^{2+}$ and $HgOH^+$ necessarily remains unsettled from the earlier work.

These results suggest rather strongly, but do not establish beyond question, that the reaction of the species $Cr(OH_2)_4(OH)Cl^+$ with Hg^{2+} rather than that of $HgOH^+$ with $Cr(OH_2)_5Cl^{2+}$ is responsible for the rate law term inversely dependent upon hydrogen ion. The ion $Cr(NH_3)_5Cl^{2+}$ in the present study is a very much weaker acid than is $Cr(OH_2)_5Cl^{2+}$, whereas it is difficult to see how $HgOH^{2+}$, comparably abundant in both studies, could discriminate drastically between the two acidic forms. It should be pointed out also that analogous hydrogen ion dependences are observed in the case of spontaneous aquation of chloroaquo and chloroammine complexes of chromium(III) and cobalt(III).

Although attempts have been made[2,9] at correlation of the rates and activation parameters of similar halide-transfer reactions with data on systems in which chloride ion transfer accompanies electron exchange, the earlier comparisons invariably involved rates or activation parameters for which complete experimental data were not available, and estimates based on analogy were employed. The present study provides data permitting a comparison of the activated complexes $[(NH_3)_5Cr\cdots Cl\cdots Hg(aq)^{4+}]^*$ and $[(NH_3)_5Cr\cdots Cl\cdots Cr(aq)^{4+}]^*$. The values of ΔS^* for formation of these activated complexes from the component ions are -13 and -27 eu,[9] respectively. Two changes affecting the first coordination spheres of the reactant complexes are impending in the transition state for the electron-exchange reaction: five ammonias are to be released by one chromium, and five water molecules are bound more strongly and more closely to the chromium which will become chromium(III). The entropy of activation will reflect the extent to which the coordination spheres of the ions, in forming the transition state, are readjusted to equalize energies for electron transfer. The former change would act to produce a more positive ΔS^*, and the latter, a more negative value. Assuming these two factors provide the main contribution to ΔS^* in the reaction of $Cr(NH_3)_5Cl^{2+}$ with Cr^{2+}, beyond those factors common to each, one concludes the increasingly tight hold of water molecules by chromium is the more important. The 14 eu by which the ΔS^* values of the two reactions differ does not appear unreasonably large to be interpreted as the net effect of such changes.

The reactions of Hg^{2+} with $Cr(NH_3)_5Cl^{2+}$ and $Cr(OH_2)_5Cl^{2+}$, considering for the latter only the rate law term independent of hydrogen ion, proceed with remarkably similar specific rates, 0.087 and 0.048 M^{-1} sec^{-1} at 25.0°. The spontaneous aquation reactions, however, differ in rate[9,11] by a factor of ~70 at the same temperature, again considering only the path independent of hydrogen ion in the case of $Cr(OH_2)_5Cl^{2+}$. In the Hg^{2+}-catalyzed aquation reactions, five of the ligands on chromium(III) exert only minor effects relative to their roles in spontaneous aquation.

[10] This program is based on a report from the Los Alamos Scientific Laboratory, LA2367 plus addenda. We are grateful to Drs. T. W. Newton and R. H. Moore for supplying us with the computer programs and to Mr. J. P. Birk for adapting them to the IBM 7074 computer facilities.

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Oxidation of Cuprous Chloride by Oxygen in Glacial Acetic Acid

BY PATRICK M. HENRY

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Cuprous chloride has long been known to be oxidized readily by oxygen to copper(II) in aqueous solutions, but, because of the speeds of the reaction, attempts to define the kinetics have been unsuccessful.[1-3] The oxidation of slurries of cuprous chloride in solvents such as acetic acid is much slower than in water. This decrease in rate is presumably at least partially due

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