sought.[17] Peaks characteristic of H_3O^+ were observed at 25° at ~1700, ~2210, and ~3000 cm.$^{-1}$ (the latter two are very broad). The Raman spectrum of the solid gave peaks at 2217 and 2231 cm.$^{-1}$. There are thus three CN stretching vibrations: 2204 cm.$^{-1}$, appearing in the infrared only; 2218 cm.$^{-1}$, appearing in the infrared and Raman; and 2231 cm.$^{-1}$, appearingin the Raman only. These are to be compared with 2189, 2198, and 2207 cm.$^{-1}$ for solid $KAu(CN)_4$.[15] The Au–C stretching frequency appears at 488 cm.$^{-1}$ compared to 461 cm.$^{-1}$ for $KAu(CN)_4$. A solution of $HAu(CN)_4$ containing an equivalent amount of added KBr was allowed to evaporate slowly at 25°. The white solid gave the infrared absorption of $KAu(CN)_4$, showing that HBr had been lost rather than HCN. However, when a Fluorolube mull of $HAu(CN)_4 \cdot 2H_2O$ was placed on a CsBr window in an attempt to observe the low-frequency spectrum, reaction with the CsBr window was observed and an Au–Br frequency appeared.

Passage of a $KAu(CN)_2Br_2$ solution through H^+ form Dowex-50 gave the $Au(CN)_2Br_2^-$ ion in aqueous solution as shown by its infrared absorption. The yellow solid $HAu(CN)_2Br_2 \cdot xH_2O$, obtained on evaporation, showed absorption at 2231 and 2215 cm.$^{-1}$.

Conclusions

Contrary to the behavior found with nickel(II), $Au(CN)_4^-$ does not add cyanide in saturated aqueous cyanide solution to form concentrations of $Au(CN)_5^{2-}$ or $Au(CN)_6^{3-}$ observable by their infrared absorption. Thus, we are faced with a situation similar to that of the reported $Cd(CN)_6^{4-}$ complex[18] which was not confirmed by infrared measurements.[9] We conclude that these higher complexes (if indeed formed) either absorb at the same frequency with the same absorption coefficient as $Au(CN)_4^-$ [or $Cd(CN)_4^{2-}$, respectively] which is unlikely, or are formed in very small concentrations. In this respect, $Au(CN)_4^-$ resembles $Pd(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$, neither of which forms pentacyanide complexes.[19]

Observation of mixed halide–cyanide complexes of Au(III) is straightforward in the infrared. These compounds react with free cyanide and heavier halides. When $Au(CN)_2X_2^-$ was treated with one equivalent of CN^-, the expected monohalide $Au(CN)_3X^-$ was not observed although the monohalides $Au(CN)_3Cl^-$ and $Au(CN)_3Br^-$ could be prepared by a different method. In aqueous solution, one might have expected $Au(CN)_3Cl^-$ to disproportionate into $Au(CN)_2Cl_2^-$ and $Au(CN)_4^-$, but this was not observed. In solution, $Au(CN)_2Cl_2^-$ is stable, yet it is not formed by the interaction of $AuCl_4^-$ and $Au(CN)_4^-$. On the other hand, metathetical reactions, involving substitution of lighter halides by heavier halides and of any halide by cyanide, occur, showing that the bound halide is somewhat labile.

Reactions followed by infrared solution studies are

$$Au(CN)_2X_2^- \ (X = Cl, Br, \text{ or } I) + 2CN^- = Au(CN)_4^- + 2X^-$$

$$Au(CN)_4^- + \text{saturated KBr} \longrightarrow \text{no reaction}$$

$$Au(CN_2)Cl_2^- + 2X^- (X^- = Br \text{ or } I) = Au(CN)_2Br_2 \text{ or } Au(CN)_2I_2$$

$$Au(CN)_2Br_2^- \xrightarrow{HSO_3^-} Au(CN)_2^-$$

$$Au(CN)_3Cl^- + Br^- = Au(CN)_3Br^- + Cl^-$$

The absorption spectrum of $HAu(CN)_4 \cdot 2H_2O$ shows clearly the absorption characteristic of H_3O^+. Thus, at least one of the two H_2O molecules in $HAu(CN)_4 \cdot 2H_2O$ is involved in proton hydration. Further, it appears that in solid $H_3O^+Au(CN)_4^- \cdot H_2O$ both the Au–C and C–N bonds are stronger than in solid $KAu(CN)_4$ or in aqueous $HAu(CN)_4$. The Au–Cl bond in $Au(CN)_3Cl^-$ is apparently slightly stronger than that in *trans*-$Au(CN)_2Cl_2^-$. The Raman and infrared spectra are consistent with a planar configuration of C_{2v} symmetry for $Au(CN)_3Cl^-$.

[17] C. C. Ferriso and D. F. Hornig, *J. Chem. Phys.*, **23**, 1464 (1955).

[18] M. Prytz and T. Osterud, *Acta Chem. Scand.*, **6**, 1534 (1952).

[19] J. M. Smith, L. H. Jones, and R. A. Penneman, unpublished work (1963).

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Substitution Reactions of Iodopentaaquochromium(III) Ion

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Received September 28, 1964

Bromide and chloride replace iodide in iodopentaaquochromium(III) ion. The reaction proceeds without intermediate formation of the hexaaquo ion. The rate of decomposition of iodopentaaquochromium(III) ion in the presence of bromide ion was found to be equal to the rate in the presence of perchlorate ion of the same acidity and ionic strength. Bromopentaaquochromium(III) ion is formed along with hexaaquochromium(III) ion at a concentration ratio of 0.127 (in 1 *M* hydrobromic acid). The results are interpreted in terms of an SN1 mechanism. Similar results were obtained in the presence of chloride. The mechanism is confirmed by the observed retardation of the reaction in the presence of iodide which is characteristic for a dissociative mechanism (mass law retardation).

Substitution reactions of octahedral complexes of the type $MA_5X + Y \rightarrow MA_5Y + X$ may be considered to proceed by an SN1 mechanism if the reaction rate is independent of the nature and concentration of the incoming ligand Y (a dependence on Y does not, however, disprove an SN1 mechanism). Another characteristic confined to SN1 reactions is the so-called mass law retardation,[1] *i.e.*, a retardation of the reaction by X which cannot be ascribed to the reversible reaction $MA_5Y + X \rightarrow MA_5X + Y$.

[1] C. K. Ingold, "Structure and Mechanism of Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 362.

The application of these criteria to reactions in aqueous solutions is often foiled by the participation of the solvent (water) in the reaction. It was observed that in some cases the reaction proceeds by the intermediate formation of an aquo complex,[2] as in the exchange of radioactive chloride ion with *cis*-$Co(en)_2Cl_2^+$.

$$Co(en)_2Cl_2^+ + H_2O \longrightarrow Co(en)_2(H_2O)Cl^{2+} + Cl^-$$
$$Co(en)_2(H_2O)Cl^{2+} + {}^*Cl^- \longrightarrow Co(en)_2{}^*Cl_2^+ + H_2O$$

Experimental rate laws cannot be applied to discriminate between SN1 and SN2 mechanisms in consecutive aquation–anation reactions of this type; however, the widely accepted generalization that "in water, aquation invariably precedes substitution by anions" is hardly justified by the few systems (mostly cobaltic and chromic ammines) that were shown to follow this scheme.[3–5]

Haim and Wilmarth[6] have shown that the substitution of N_3^- by NCS^- in $Co(CN)_5N_3^{3-}$ does not proceed with intermediate formation of $Co(CN)_5H_2O^{2-}$. Water and thiocyanate were shown to compete for the same intermediate, $Co(CN)_5^{2-}$, which was formed by loss of azide from the reactant. Haim and Taube[7] found evidence of formation of the intermediate $Co(NH_3)_5^{3+}$ in substitution reactions of cobalt ammines. It has lately been shown that ligand–ligand replacement occurs in iodopentaaquochromium(III) ion where iodide is replaced by chloride without prior formation of hexaaquochromium(III) ion.[8]

The object of the present investigation was to study the effect of the incoming ligand on the rate of decomposition of $Cr(H_2O)_5I^{2+}$ and on the nature of the reaction products. The relatively rapid rate of the reaction (half-life 50 min. at 30° in 1 *M* perchloric acid) and the thermodynamic instability of this complex ion make this ion especially suitable for this purpose.

Experimental

Materials.—Iodopentaaquochromium(III) ion was prepared by oxidation of chromous perchlorate solutions by iodine.[9] Chromous perchlorate ($\sim$0.5 *M*) in perchloric acid ($\sim$0.5 *M*), was prepared by electrolytic reduction of chromic perchlorate on a mercury cathode (current density 0.5 amp./dm.^{2}) and stored under nitrogen. De-aerated, acidified solutions of potassium iodate with a slight excess of potassium iodide were titrated with chromous perchlorate. The resulting solutions, containing CrI^{2+} with some free iodide and traces of hexaaquochromium(III) ion and chromic dimer,[10] were absorbed on a cation-exchange column of 2-cm. diameter and 5-cm. height, containing Dowex 50X4, 100–200 mesh. This column was cooled by circulating ice water; the temperature within the column was below 1.0°. Elution was carried out with 0.4 *M* perchloric acid, and the resulting solution contained CrI^{2+} ($\sim$0.01 *M*) in perchloric acid ($\sim$0.25 *M*). All reagents were of A.R. quality. Triple distilled water was used throughout.

Kinetic Measurements.—The change of the optical density of the solution at 650 mμ was measured with an Optica Milano CF-4 spectrophotometer. Cells of 3-cm. optical path in a thermostated cell holder were used. The temperature was kept at 30 ± 0.1° by circulating water from a thermostat. The solutions were prepared by addition of 5 ml. of the chromic solution to 20 ml. of a solution containing perchloric, hydrobromic, or hydriodic acid and their sodium salts at a total concentration of 1.25 *M*. The solutions were kept in the thermostat for 2 min. Part of the solution was then transferred to the optical cells and the rest was kept in the thermostat for product analysis. D_∞ was measured after a period of seven or more half-lives (its magnitude was about 10% of D_0). The first-order rate constant k was measured from plots of log $(D_t - D_\infty)$ *vs.* t. The reproducibility was better than 2%.

Separation of Products.—The reaction products (10 or 15 ml.) were diluted with water (1:5) after seven or more half-lives and absorbed on cooled cation-exchange columns (Dowex 50X8). The halopentaaquochromium(III) ion was eluted with 1 *M* perchloric acid and the hexaaquochromium(III) ion with 2 *M* acid.

Analysis of Chromium.—Aliquots of the separated products and of the original solution were oxidized to chromate by alkaline hydrogen peroxide and the optical density was measured at 372 mμ with a Beckman B spectrophotometer.[11] The difference between the concentration of the original solution and the sum of the separated products was less than 1.5% in all experiments.

Results and Discussion

The Reaction in Perchloric Acid.—The decomposition of CrI^{2+} is a first-order reaction at constant $[H^+]$. The rate constant k, measured from the plot of log $(D_t - D_\infty)$ *vs.* t, decreases with increasing hydrogen ion concentration. The change of k with $[H^+]$ at 30° and ionic strength $I = 1.07$ *M* is presented in Table I. The rate constant k is a linear function of $1/[H^+]$, $k = k_0 + k_a/[H^+]$. The values of k_0 and k_a, determined from the plot of k *vs.* $1/[H^+]$, are $k_0 = 1.52 \times 10^{-4}$ sec.$^{-1}$, $k_a = 8.17 \times 10^{-5}$ sec.$^{-1}$ at 30° and $I = 1.07$ *M*.

TABLE I

RATE CONSTANTS IN PERCHLORIC ACID–SODIUM PERCHLORATE MEDIUM ($I = 1.07$ *M* at 30°)

$[H^+]$, *M*	0.26	0.46	0.66	0.86	1.06
10^4k, sec.$^{-1}$	4.65	3.30	2.72	2.42	2.30

After the conclusion of this part of the work, a detailed investigation of the aquation of CrI^{2+} in perchloric acid was published by Espenson.[12] His data, which also include the enthalpy and entropy of activation for the two reaction paths, are in agreement with the findings reported here. The values of k_0 and k_a calculated from data of ref. 12 are 1.65×10^{-4} sec.$^{-1}$ and 7.17×10^{-5} sec.$^{-1}$, respectively, at 30° and $I = 1.00$ *M*.

Decomposition Rates and Reaction Products in the Presence of Halide Ions.—The products of decomposition of CrI^{2+} in the presence of chloride and bromide were separated by ion-exchange chromatography and were found to contain considerable amounts of chloropentaaquochromium(III) and bromopentaaquochromium(III), respectively. The first-order rate constants of decomposition of CrI^{2+} were measured in

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[2] G. W. Ettle and C. H. Johnson, *J. Chem. Soc.*, 1490 (1939).

[3] D. R. Stranks, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 136.

[4] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

[5] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, p. 551.

[6] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573, 583 (1962).

[7] A. Haim and H. Taube, *ibid.*, **2**, 1199 (1963).

[8] M. Ardon, *Proc. Chem. Soc.*, 333 (1964).

[9] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

[10] M. Ardon and R. A. Plane, *ibid.*, **81**, 3197 (1959).

[11] G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

[12] J. H. Espenson, *Inorg. Chem.*, **3**, 968 (1964).

TABLE II

DECOMPOSITION RATES AND PRODUCTS IN THE PRESENCE OF HALIDE IONS (I = 1.07 M at 30°)

Expt. no.	$[X^-]$, M	$[H^+]$, M	No. of runs	10^4k, sec.$^{-1}$	R	R_{cor}	k_x/k_{H_2O}
1	Br^- 1.00	1.06	4	2.32	0.102	0.127	0.21
2	Br^- 0.50	1.06	2	2.33	0.059	0.074	0.23
3	Br^- 1.00	0.46	2	3.32	0.085	0.102	0.24
4	I^- 1.00	1.06	3	2.03			0.24
5	I^- 0.70	1.06	2	2.08			
6	I^- 0.30	1.06	3	2.22			
7	I^- 1.00	0.46	2	3.03			
8	Cl^- 1.00	1.06	8	2.45	0.143		0.24
9	Cl^- 0.80	1.06	2	2.43	0.113		0.23
10	Cl^- 0.60	1.06	2	2.38	0.089		0.24
11	Cl^- 1.00	0.46	2	3.42	0.091		0.26

the presence of varying concentrations of H^+ and X^- (X = Cl, Br, I). A constant ionic strength of 1.07 M was maintained by addition of sodium perchlorate.

Table II presents the results of the kinetic measurements and the concentration ratio $R = [CrX^{2+}]/[Cr(H_2O)_6{}^{3+}]$ of the reaction products.

The Reaction in the Presence of Bromide.—The rate constants of decomposition of CrI^{2+} in the presence of varying concentrations of Br^- and H^+ are given in expt. 1–3 (Table II). A comparison with the data of Table I reveals that the rate of decomposition is not changed by the replacement of perchlorate with bromide.

The products of the reaction contain an appreciable concentration of the bromopentaaquochromium(III) ion. This ion is thermodynamically unstable: the equilibrium quotient $Q = [CrBr^{2+}]/[Cr^{3+}][Br^-]$ is equal to 2.6×10^{-3} at 30° and $I = 2.0$ M.[13] The equilibrium ratio is $R_{eq} \backsim 3 \times 10^{-3}$ under the conditions of expt. 1, whereas the experimental value is $R = 0.102$. This result can be rationalized only by assuming a substitution of iodide by bromide without the intermediate formation of $Cr(H_2O)_6{}^{3+}$. Part of the $CrBr^{2+}$ formed in the reaction is aquated during the time required to complete the aquation of CrI^{2+} (7–8 half-lives). The decomposition rate of $CrBr^{2+}$ is known from the work of Guthrie and King[14] (*e.g.*, under the conditions of expt. 1 the first-order rate constant is equal to 1.01×10^{-5} sec.$^{-1}$). The initial product ratio R_{cor} is higher than the ratio R, found at the end of the reaction, and is equal to

$$R_{cor} = \frac{[CrBr^{2+}] + \Delta[CrBr^{2+}]}{[Cr^{3+}] - \Delta[CrBr^{2+}]}$$

where $\Delta[CrBr^{2+}]$ is the concentration of $CrBr^{2+}$ that was aquated during the reaction time t (2.4×10^4 sec. in expt. 1 and 2 and 1.7×10^4 sec. in expt. 3). The quantity $\Delta[CrBr^{2+}]$ was calculated from

$$\frac{[CrBr^{2+}]}{[CrBr^{2+}] + \Delta[CrBr^{2+}]} = \frac{k_1}{k_2 - k_1}\left(e^{-k_1t} - e^{-k_2t}\right)$$

where k_1 and k_2 are the rate constants for aquation of CrI^{2+} and $CrBr^{2+}$, respectively. The corrected values R_{cor} are given in Table II.

The fact that bromide replaces iodide without changing the decomposition rate of CrI^{2+} strongly supports an SN1 mechanism with the intermediate formation of $Cr(H_2O)_5{}^{3+}$. Water and Br^- compete for this intermediate.

$$Cr(H_2O)_5I^{2+} \xrightarrow{k_0} Cr(H_2O)_5{}^{3+} + I^-$$

$$Cr(H_2O)_5{}^{3+} + H_2O \xrightarrow{k_{H_2O}} Cr(H_2O)_6{}^{3+}$$

$$Cr(H_2O)_5{}^{3+} + Br^- \xrightarrow{k_{Br}} Cr(H_2O)_5Br^{2+}$$

The expected product ratio R is proportional to the bromide concentration, in agreement with expt. 1 and 2. Substitution of bromide is confined to the acid-independent path and does not occur in the acid-dependent path, which is responsible for 34% of the over-all reaction at $[H^+] = 1.06$ M and for 54% at $[H^+] = 0.46$ M. The product ratio varies accordingly (expt. 1 and 3). The product ratio of the acid-independent path is equal to k_{Br}/k_{H_2O}. By subtracting the portion of $Cr[H_2O]_6{}^{3+}$ produced by the acid-dependent path from the total chromic products, the ratio k_{Br}/k_{H_2O} can be estimated (Table II, last column).[15]

Mass Law Retardation by Iodide.—The concentration of free iodide in expt. 1–3 and 8–11 is very small ($<5 \times 10^{-3}$ M). High iodide concentrations decrease the decomposition rate of CrI^{2+} (expt. 4–7). This effect of iodide cannot be the result of the reverse reaction $Cr(H_2O)_6{}^{3+} + I^- \rightarrow Cr(H_2O)_5I^{2+} + H_2O$ since this reaction does not occur to any measurable extent. The stability constant of CrI^{2+} is too small to be measured and is certainly smaller than that of $CrBr^{2+}$. A decrease in the decomposition rate of CrI^{2+} by iodide under these conditions is irreconcilable with an SN2 mechanism. It is the result of a mass law retardation of the rate-determining step and confirms the dissociative mechanism

$$Cr(H_2O)_5I^{2+} \underset{k_I}{\overset{k_0}{\rightleftharpoons}} Cr(H_2O)_5{}^{3+} + I^-$$

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(13) J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960).

(14) F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).

(15) A referee has pointed out that the rate constant for water exchange in $Cr(H_2O)_6{}^{3+}$ by an SN1 mechanism, calculated from k_{Br}/k_{H_2O} and Q, is much smaller than the experimental value of 4×10^{-6} sec.$^{-1}$ (by a factor of 40). This argument may support an SN2 mechanism for the exchange reaction as suggested in ref. 16.

(16) R. J. Baltisberger and E. L. King, *J. Am. Chem. Soc.*, **86**, 795 (1964).

$$\mathrm{Cr(H_2O)_5}^{3+} + \mathrm{H_2O} \xrightarrow{k_{\mathrm{H_2O}}} \mathrm{Cr(H_2O)_6}^{3+}$$

This mechanism accounts for the observed retardation: if the steady-state condition $d[\mathrm{Cr(H_2O)_5}^{3+}]/dt = 0$ is assumed, it follows that

$$-\frac{d[\mathrm{CrI}^{2+}]}{dt} = k_{\mathrm{H_2O}}[\mathrm{Cr(H_2O)_5}^{3+}] = \frac{k_{\mathrm{H_2O}}k_0}{k_{\mathrm{I}}[\mathrm{I}^-] + k_{\mathrm{H_2O}}}[\mathrm{CrI}^{2+}] = k[\mathrm{CrI}^{2+}]$$

Hence, the rate constant k is decreased by iodide. This effect will be negligible only if $k_{\mathrm{I}}[\mathrm{I}] \ll k_{\mathrm{H_2O}}$; this condition is realized in expt. 1–3 and 8–11, where the iodide concentration is smaller than 5×10^{-3} M. The results of expt. 4–7 were used to evaluate $k_{\mathrm{I}}/k_{\mathrm{H_2O}}$: the plot of $1/k$ *vs.* $[\mathrm{I}^-]$ yields a straight line. The quantity $1/k_0$ measured from the graph is equal to $1/k_0$ measured in perchloric acid (1.52×10^{-4} sec.$^{-1}$). The ratio $k_{\mathrm{I}}/k_{\mathrm{H_2O}}$ is equal to 0.24.

The Reaction in the Presence of Chloride.—The equilibrium quotient $Q = [\mathrm{CrCl}^{2+}]/[\mathrm{Cr}^{3+}][\mathrm{Cl}^-]$ is equal to 0.086 at 30° and an ionic strength of 0.959.[16] Hence the equilibrium ratio is $R_{\mathrm{eq}} \sim 0.086$ under the conditions of expt. 8. Formation of CrCl^{2+} during the decomposition of CrI^{2+} cannot be attributed to the anation of $\mathrm{Cr(H_2O)_6}^{3+}$, since this reaction is much too slow—the second-order rate constant[16] is $\sim 1.6 \times 10^{-7}$ l. mole^{-1} sec.$^{-1}$ under the conditions of expt. 8. It has been shown[8] that this reaction is not catalyzed by the decomposition products of CrI^{2+}, hence it was concluded that in this case, as in the presence of bromide, CrCl^{2+} is formed by direct substitution of iodide.

Replacement of perchlorate by chloride causes a slight but significant increase in the decomposition rate of CrI^{2+} (6.5% in hydrochloric acid, 1 M). This specific effect of chloride may be due to the existence of ion pairs which weaken the Cr–I bond. Alternatively, the effect might be attributed to a small contribution of a bimolecular reaction path. Even if the latter assumption is made, the expected product ratio $[\mathrm{CrCl}^{2+}]/[\mathrm{Cr(H_2O)_6}^{3+}]$ should be less than 0.065 at $[\mathrm{Cl}^-] = 1$ while the experimental value is 0.143. An SN2 reaction path could not account for the greater portion of CrCl^{2+} produced in the reaction, and it is necessary to assume an SN1 mechanism similar to that operating in bromide solutions. Experiments 8–11 reveal that the dependence of the product ratio on $[\mathrm{Cl}^-]$ and $[\mathrm{H}^+]$ is similar to that found in bromide solutions. No correction for aquation of CrCl^{2+} is necessary because of the low rate of this reaction[16]—the first-order rate constant is $\sim 13 \times 10^{-7}$ sec.$^{-1}$. The ratios $k_{\mathrm{Cl}}/k_{\mathrm{H_2O}}$ were calculated by assuming that the reaction proceeds solely by an SN1 mechanism.

Comparison of the ratios $k_{\mathrm{X}}/k_{\mathrm{H_2O}}$ for chloride, bromide, and iodide (Table II) reveals that these ions do not differ considerably in their ability to compete with water for the intermediate $\mathrm{Cr(H_2O)_5}^{3+}$.

The effect of anions on the decomposition of CrBr^{2+} and CrCl^{2+} is now being investigated, by following the method outlined here.

Acknowledgment.—The author wishes to thank Dr. B. Perlmutter-Hayman for helpful discussion of the results.

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Synthesis of Chelating Agents. III.[1] Chelating Behavior of Keto Derivatives of Iminodiacetic Acids

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Received February 13, 1964

ω-Aminoacetophenone-N,N-diacetic acid (AAPDA) and 2-glycylthiophene-N,N-diacetic acid (GTDA) have been synthesized and the stoichiometric stability constants of their proton and metal complexes have been measured potentiometrically at 25° in a medium of constant ionic strength of 0.10 M. The 1:1 chelates of both ligands show nearly the same stability for the metal ions chosen, and the order of relative stabilities is Cu(II) > Ni(II) > Cd(II) ≈ Zn(II) > Co(II) > Ca(II) > Sr(II) > Mg(II). The formation of 1:2 chelates is also observed for Cu(II), Ni(II), Cd(II), Zn(II), and Co(II). By comparing their stability constants with those of aminoacetone-N,N-diacetic acid (AADA), the formation of a stronger coordination bond with carbonyl oxygen is suggested for AAPDA and GTDA than for AADA.

Introduction

In the previous paper[1] the synthesis and the chelating behavior of aminoacetone-N,N-diacetic acid (AADA) (I) have been reported, and it was proved that the carbonyl oxygen of the ligand contributed to the coordination for a certain group of metal ions.

In the present investigation, ω-aminoacetophenone-N,N-diacetic acid (AAPDA) (II) and 2-glycylthiophene-N,N-diacetic acid (GTDA) (III) have been synthesized and their chelating behaviors investigated in order to understand the effect of the substitution of the methyl group α to the carbonyl carbon atom with aromatic rings.

[1] Paper II: T. Ando, *Bull. Chem. Soc. Japan*, **36**, 1593 (1963).