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Properties of the Acidocobaltammines. I. The Chlorotriammine Series[1]

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The consecutive constants of formation of chlorodiaquo- and dichloroaquo-ions from triaquotriamminecobalt(III) were determined at 0° and 25°. Similar constants were determined for the triaquoethylenediamineamminecobalt(III) system. No difference in the heats of binding between the chloride and cobalt ions were found for the two systems nor between the Co(III) ions containing one or two chloride ions. The differences in the various constants are due to differences in the entropies of the systems.

In order to compare the effect of substituting an ethylenediamine molecule for two ammonia molecules on the properties of cobaltammines, Werner and Grun[3] prepared several triamminecobalt(III) and ethylenediamineamminecobalt(III) compounds. In each case the starting material was the respective dichloro chloride. As a result of their experiments Werner and Grun concluded that the replacement of two ammonia molecules in the ammonia system by an ethylenediamine molecule decreased the stability of the Co(III) complex and permitted a greater mobility of the complexly bound acido group, *i.e.*, the chloride ion.

In the present paper the relative strength of the bond between the Cl ion and the cobalt ion for the two systems has been calculated from the equilibrium constants for the triaquo, chlorodiaquo and dichloroaquo ion at 0° and 25°. The equilibrium constants have been determined spectrophotometrically by making use of the extinction coefficients of the cobaltammines in the visible region. Because of the difficulty of obtaining reproducible absorption spectra of the chlorodiaquo and, in particular, the dichloroaquo ions, it was necessary to determine the equilibrium constants by using the method of Bjerrum.[4]

Experimental

Materials.—Erdmann's salt,[5] $NH_4[Co(NH_3)_2(NO_2)_4]$, was used as the starting material for preparing the other cobaltammines. It was converted into trinitrotriamminecobalt(III) by dissolving it in water containing ammonium carbonate. A rapid stream of air was then passed through the solution while it was being heated on a boiling water-bath. Additional ammonium carbonate was added from time to time during the first half-hour. After all of the ammonia has been expelled, the solution is cooled and trinitrotriamminecobalt(III) is deposited as bright orange needles. In this way the presence of nitrate or chloride ions is prevented so that the slightly soluble *trans*-dinitrotetramminecobalt(III) nitrate or chloride does not form. Dichloroaquotriamminecobalt(III) chloride and chlorodiaquotriamminecobalt(III) chloride were prepared from trinitrotriamminecobalt(III) by the methods described by Jorgensen.[6] The same salts of the ethylenediamine system were prepared by the methods of Werner and Grun.[1]

Tenth molal solutions of the triaquo perchlorate salts of both systems in hundredth molar perchloric acid were prepared by treating the respective dichloro salts with a stoichiometric amount of silver perchlorate.

Analytical.—Each of the cobaltammines was analyzed for cobalt and chloride by methods previously described.[7]

Solutions of salts of both systems can also be analyzed for Co(III) by titrating with Fe(II) in acid solutions at room temperature. The reactions are rapid and a sharp end-point is obtained which can be determined potentiometrically. Tetramminecobalt(III) salts, the most likely impurities to be present, were not reduced at room temperature and only slowly at 85°.

Apparatus and Procedure.—The optical densities were measured over the range 350–700 mμ with a Beckman quartz spectrophotometer using 1 cm. cells (see Fig. 1). The wave lengths used for the equilibrium measurements were 430, 480, 525, 600 and 660 mμ for the ammonia system and 430, 480, 540, 600 and 660 mμ for the ethylenediamine system.

The Co(III) concentration of each solution was 1×10^{-2} molal for the ammonia system and 5×10^{-3} molal for the ethylenediamine system. Each solution contained hundredth molal perchloric acid to prevent the formation of hydroxocobalt(III) ions and had a total ionic strength of 5 molal. The source of chloride ion was sodium chloride while the inert salt was sodium perchlorate. Each of the equilibrium solutions was kept in a constant temperature

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[1] In part from the thesis submitted by Richard G. Yalman to the Graduate School of Arts and Sciences of Harvard University in February, 1949, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Deceased May 15, 1952.

[3] A. Werner and A. Grun, *Ber.*, **37**, 4704 (1904); **38**, 4035 (1905).

[4] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[5] O. Erdmann, *J. prakt. Chem.*, **97**, 410 (1866).

[6] S. M. Jorgensen, *Z. anorg. Chem.*, **11**, 434 (1896).

[7] A. B. Lamb and E. B. Damon, THIS JOURNAL, **59**, 383 (1937).

bath at the desired temperature (0° and 25°) until measurements made on successive days agreed within 0.5%. At the end of a week slight decomposition had occurred in solutions of the ammonia system containing 4 molal sodium chloride while considerable decomposition and the formation of chlorine were observed in five molal sodium chloride. The ethylenediamine system appeared to be completely stable in five molal sodium chloride.

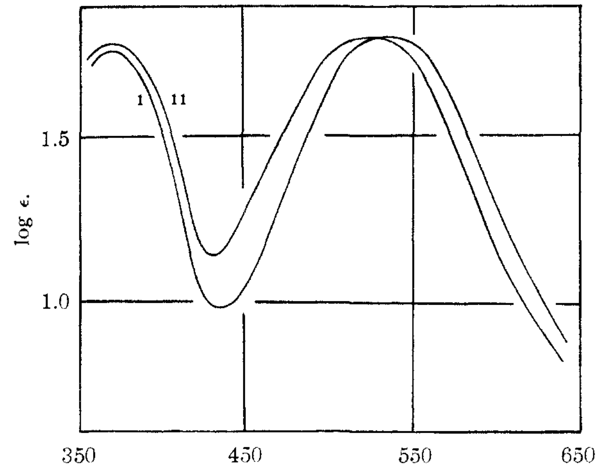

Fig. 1.—Absorption spectra of the cobalt triammines: I. triaquotriamminecobalt(III); II, triaquoethylenediamineamminecobalt(III).

Calculation of Constants

The equilibrium constants (consecutive constants) for the formation of the dichloroaquo ions from the triaquo ions are determined by the equilibria

$$\mathrm{Co(NH_3)_3(H_2O)_3^{+++} + Cl^- = Co(NH_3)_3(H_2O)_2Cl^{++} + H_2O}$$

$$K_1 = [\mathrm{Co(NH_3)_3(H_2O)_2Cl^{++}}]/[\mathrm{Co(NH_3)_3(H_2O)_3^{+++}}][\mathrm{Cl^-}] \quad (1)$$

$$\mathrm{Co(NH_3)_3(H_2O)_2Cl^{++} + Cl^- = Co(NH_3)_3H_2OCl_2^{+} + H_2O}$$

$$K_2 = [\mathrm{Co(NH_3)_3H_2OC_2^{+}}]/[\mathrm{Co(NH_3)_3(H_2O)_2Cl^{++}}][\mathrm{Cl^-}] \quad (2)$$

Although the total ionic strength in all of the solutions investigated remained constant, the interchanging of chloride and perchlorate ions will produce specific ionic effects. In view of the similarity between the ammonia and ethylenediamine systems and because we are only interested in determining the relative values of the equilibrium constants, we are neglecting these effects in our calculations and are assuming that the activity coefficients of the Co(III) ions remain constant. In the same way the concentration of water, which should be found on the right hand side of the above expressions, is assumed to be constant and is incorporated within the values obtained for the equilibrium constants.

If the optical densities of the Co(III) solutions is an additive function of the optical density of the individual Co(III) ions present and if Beer's law holds true for these solutions, then the optical density observed is related to the extinction coefficients and molal concentrations of the various ions present by

$$D = \epsilon_1 M_1 + \epsilon_2 M_2 + \epsilon_3 M_3 \quad (3)$$

At any given wave length and chloride ion concentration D is the observed optical density and ϵ_1, ϵ_2, ϵ_3, M_1, M_2 and M_3 are the extinction coefficients and molal concentrations of the triaquo, chlorodiaquo and dichloro aquo ions, respectively. Since $M_1 + M_2 + M_3 = M_0$, the total Co(III) concentration, and the relationships between M_1, M_2, M_3, K_1 and K_2 are known from equations (1) and (2), then by substituting in (3) we can obtain an expression for the optical density of the solution in terms of one variable, the chloride ion concentration.

$$D = M_0 \frac{\epsilon_1}{(1 + K_1[\mathrm{Cl^-}] + K_1K_2[\mathrm{Cl^-}]^2)} + \epsilon_2K_1[\mathrm{Cl^-}] + \epsilon_3K_1K_2[\mathrm{Cl^-}]^2 \quad (4)$$

Upon rearranging we get

$$D - M_0\epsilon_1 = M_0\epsilon_2K_1[\mathrm{Cl^-}] + M_0\epsilon_3K_1K_2[\mathrm{Cl^-}]^2 - DK_1[\mathrm{Cl^-}] - DK_1K_2[\mathrm{Cl^-}]^2 \quad (5)$$

The term on the left in equation (5) was obtained from the optical density of the equilibrium solutions and the molal extinction coefficients for the triaquo Co(III) ions. The term on the right is linear in the four, but unknown, coefficients ϵ_2K_1, $\epsilon_3K_1K_2$, K_1K_2 and K_1. From the values of the optical densities of the equilibrium solutions at four different chloride ion concentrations, four simultaneous equations were obtained. Their solutions gave the desired values of K_1 and K_2.

Results

The absorption curves for the two systems are shown in Fig. 1. The validity of Beer's law for the five wave lengths chosen for the examination of each system was verified by examining solutions containing different concentrations of the triaquocobalt(III) ions. The establishment of a true equilibrium between the three ions of the ammonia system was determined by measuring the optical densities of solutions of Co(III) from three different sources in 4 molal sodium chloride. The resulting data are collected in Table I.

TABLE I

Source of Co(III)	Wave length in mμ				
	430	480	525	600	660
$\mathrm{[Co(NH_3)_3H_2OCl_2]Cl}$	27.2	20.5	40.5	36.1	21.6
$\mathrm{[Co(NH_3)_3(H_2O)_2Cl]Cl_2}$	27.0	20.5	40.4	36.0	20.4
$\mathrm{[Co(NH_3)_3(H_2O)_3](ClO_4)_3}$	27.1	20.4	40.4	36.1	21.4

A summary of similar data obtained at each of the chloride ion concentrations for both systems is given in Tables II and III. Values of K_1 and K_2 calculated from the data for each of the wave lengths are also given in Tables II and III. No explanation is offered for the apparently systematic variation of K_1 with a change in the wave length. The same variation in K_2, however, would be expected since the calculation of K_2 is dependent upon the value of K_1.

Table IV gives the average values of the equilibrium constants at 0° for the two systems. The same variation for the values of the equilibrium constants at the different wave lengths was found at this temperature as at 25°.

The free energy, heat of reaction and the entropy changes were calculated at 25° using the data in Tables III and IV and are included in Table V. The values reported here are only relative and are dependent upon the assumption that the

TABLE II

EXTINCTION COEFFICIENTS OF AMMONIA SYSTEM AT 25°

Molar concn. NaCl	Wave length in mμ				
	430	480	525	600	660
0	10.5	36.8	71.2	21.7	4.2
1	15.3	25.3	50.4	29.6	10.9
2	19.9	22.1	49.3	34.5	15.9
3	24.9	21.6	43.8	35.4	18.4
4	27.1	20.5	40.4	36.1	21.4
K_1	1.1	0.9	0.8	1.0	1.3
$K_2 \times 10$	1.2	1.0	1.0	0.9	1.2

TABLE III

EXTINCTION COEFFICIENTS OF ETHYLENEDIAMINE SYSTEM AT 25°

Molar concn. NaCl	Wave length in mμ				
	430	480	540	600	660
0	7.5	24.6	31.2	7.65	1.50
2	28.5	31.7	53.7	35.1	17.2
3	29.3	28.8	50.1	35.6	20.1
4	32.4	27.8	47.3	37.9	21.0
5	35.2	28.1	48.6	41.0	23.7
$K_1 \times 10$	2.5	2.3	2.1	2.2	2.4
$K_2 \times 10^2$	2.1	1.8	1.4	1.7	2.2

TABLE IV

EQUILIBRIUM CONSTANTS AT 0°

System	$K_1 \times 10$	$K_2 \times 10^2$
Ammonia	3.0	3.4
en	0.66	0.64

activity coefficients of the Co(III) ions remained constant. However, they can be used to make comparisons between the two systems.

The smaller value for the free energy of formation for the ammonia system is in agreement with Werner and Grun's qualitative statement that the anions are more tightly bound to the cobalt atom in this system than they are in the ethylenediamine system. However, the heats of reaction for the two systems are essentially the same. Furthermore, the heat of reaction involved in introducing a second chloride ion is the same as that involved in the first chloride ion. These results might be expected since the Co–Cl bond is covalent[8] in the cobaltammines.

The large positive values obtained for the change in entropy of the two systems is due to a change in the number and magnitude of the ions involved. The decrease in charge of the Co(III) complex ion from three to two and then to one together with a simultaneous removal of chloride ions from the solution will decrease the magnitude of the forces exerted on the water molecules which will now be able to occupy a larger volume in the solution and the entropy of the system will increase.[9]

TABLE V

FREE ENERGY OF FORMATION, HEAT OF REACTION AND ENTROPY CHANGE AT 25°

Ion formed	F, cal.	H, ±500 cal.	S, ±1 cal.
$Co(NH_3)_3(H_2O)_2Cl$	−12	7600	25.5
$Co(NH_3)_3H_2OCl_2$	1300	7000	19
$CoNH_3$ en $(H_2O)_2Cl$	870	7200	21
$CoNH_3$ en H_2OCl_2	2500	6900	15

The replacement of two ammonia molecules by an ethylenediamine molecule will have little effect on the orientation of the surrounding water molecules. The observed difference in the entropy change for the ammonia and ethylenediamine systems, however, might be due to the larger ethylenediamine molecule which fixes the relative position of two Co–N bonds and decreases the number of possible positions that the chloride ion can attack the complex radical. Furthermore, if in the reactions of the complex ions a rearrangement of bonds occurs,[10] then the presence of the ethylenediamine molecule will decrease the possible number of these rearrangements. The observed differences in the entropy changes corresponding to equation (1) and (2) for the two systems is in the direction and of the magnitude that might be expected from these considerations.

Although the procedure used in this paper cannot distinguish between *cis* and *trans* isomers, the results reported here correspond to the gross equilibrium constants for the ions investigated and will give a true picture of the relative strength of the Co–Cl bond in the two triammine systems. Work is now in progress to determine the differences in the strength of the Co–Cl bond in the isomers of the tetrammine systems.

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