

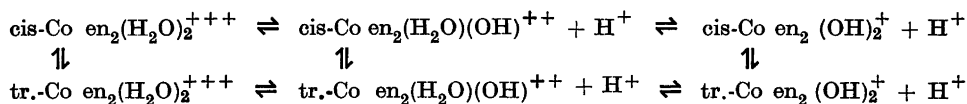
Metal Ammine Formation in Aqueous Solution

VIII. Acid-base, cis-trans, and complex equilibria in the cobalt(III)-ethylenediamine system

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In this paper the following system of acid-base and cis-trans equilibria in solutions of diaquobis(ethylenediamine)cobalt(III) salt



has been examined by means of spectrophotometric and glass electrode measurements. Further the hydrolysis constant

$$k_{h,1} = \frac{[\text{Co en}_2(\text{OH})_2^+] [\text{en}]}{[\text{Co en}_3^{+++}] [\text{OH}^-]^2} \quad (1)$$

for the exchange of one ethylenediamine molecule in the luteo complex with two hydroxyl ions has been determined by optical analysis of alkaline complex solutions in which the equilibrium was established by using charcoal as a catalyst^{1, 2}. The hydrolysis constant found ($k_{h,1} = 1.76$ liter/mol) combined with the acid-base and cis-trans constants obtained for the bis(ethylenediamine) system, gives the following values for the two 3rd formation constants in the cobalt(III)-ethylenediamine system:

$$k_3(\text{cis}) = \frac{[\text{Co en}_3^{+++}]}{[\text{cis-Co en}_2(\text{H}_2\text{O})_2^{+++}] [\text{en}]} = 10^{13.28} \quad (2)$$

$$k_3(\text{tr.}) = 10^{15.24}$$

The absorption spectra of the two isomeric diaquobis(ethylenediamine) cobalt(III) ions have previously been measured by several investigators³⁻⁵. Uspensky and Tschibisoff³ made measurements at 0° C. to diminish the velocity of the establishment of the cis-trans equilibrium, which adjusts itself spontaneously at a measurable rate in aqueous solution. Uemura and Hirasawa⁴ and Basolo⁵ also gave some data for the influence of changes in pH. The authors mentioned examined the chlorides and bromides. To avoid halogeno complex formation, nitrates have been used here, and in order to exclude salt effects a constant salt medium of 1 *N* NaNO₃ was used. The equilibria were examined at 25° C.

The two acidic dissociation constants for the cis-diaquobis(ethylenediamine) ions are given by

$$k_{s,1}(\text{cis}) = \frac{[\text{H}^+] [\text{cis-Co en}_2(\text{H}_2\text{O})(\text{OH})^{++}]}{[\text{cis-Co en}_2(\text{H}_2\text{O})_2^{+++}]}, \quad (3)$$

$$k_{s,2}(\text{cis}) = \frac{[\text{H}^+] [\text{cis-Co en}_2(\text{OH})_2^+]}{[\text{cis-Co en}_2(\text{H}_2\text{O})(\text{OH})^{++}]}$$

and analogously $k_{s,1}(\text{tr.})$ and $k_{s,2}(\text{tr.})$ denote the acidic dissociation constants for the trans-diaquo ion. The constants for the cis-trans equilibrium of the diaquo, the aquohydroxo and the dihydroxo ions will be denoted by

$$q_0 = \frac{[\text{cis-Co en}_2(\text{H}_2\text{O})_2^{+++}]}{[\text{tr.-Co en}_2(\text{H}_2\text{O})_2^{+++}]}, \quad q_1 = \frac{[\text{cis-Co en}_2(\text{H}_2\text{O})(\text{OH})^{++}]}{[\text{tr.-Co en}_2(\text{H}_2\text{O})(\text{OH})^{++}]}, \quad (4)$$

$$q_2 = \frac{[\text{cis-Co en}_2(\text{OH})_2^+]}{[\text{tr.-Co en}_2(\text{OH})_2^+]}$$

and finally for the gross acidic dissociation constants for solutions in cis-trans equilibrium, we will introduce

$$k_{s,1}(\text{gr.}) = \frac{[\text{H}^+] ([\text{cis-Co en}_2(\text{H}_2\text{O})(\text{OH})^{++}] + [\text{tr.-Co en}_2(\text{H}_2\text{O})(\text{OH})^{++}])}{[\text{cis-Co en}_2(\text{H}_2\text{O})_2^{+++}] + [\text{tr.-Co en}_2(\text{H}_2\text{O})_2^{+++}]} \quad (5)$$

$$k_{s,2}(\text{gr.}) = \frac{[\text{H}^+] ([\text{cis-Co en}_2(\text{OH})_2^+] + [\text{tr.-Co en}_2(\text{OH})_2^+])}{[\text{cis-Co en}_2(\text{H}_2\text{O})(\text{OH})^{++}] + [\text{tr.-Co en}_2(\text{H}_2\text{O})(\text{OH})^{++}]}$$

Among the 6 acidic dissociation constants and the 3 cis-trans equilibrium constants, q_0 , q_1 and q_2 , we have four independent relations

$$\begin{aligned}
 q_0 &= \frac{k_{s,1}(\text{tr.}) - k_{s,1}(\text{gr.})}{k_{s,1}(\text{gr.}) - k_{s,1}(\text{cis})} = \frac{k_{s,1}(\text{tr.}) \cdot k_{s,2}(\text{tr.})}{k_{s,1}(\text{cis}) \cdot k_{s,2}(\text{cis})} \cdot q_2 \\
 q_1 &= \frac{k_{s,2}(\text{tr.}) - k_{s,2}(\text{gr.})}{k_{s,2}(\text{gr.}) - k_{s,2}(\text{cis})} = \frac{k_{s,2}(\text{tr.})}{k_{s,2}(\text{cis})} \cdot q_2
 \end{aligned}
 \tag{6}$$

As a consequence of these relations, knowledge of five of the constants is enough to calculate the remaining four. In this investigation all 6 acidic dissociation constants were estimated by means of glass electrode measurements, and the constant q_2 was determined by means of spectrophotometric measurements. The two other cis-trans constants, q_0 and q_1 , therefore, could be estimated in different ways. The most reliable values were calculated by combining the direct determined value for q_2 with the expressions containing the products of the acidic dissociation constants, and all experimental data showed satisfactory agreement within the uncertainty of the experiments. For the 9 mass action constants, which govern the system, the following values were found in 1 *N* NaNO₃ at 25° C:

$$\begin{aligned}
 k_{s,1}(\text{cis}) &= 10^{-6.06}, & k_{s,2}(\text{cis}) &= 10^{-8.19} \\
 k_{s,1}(\text{tr.}) &= 10^{-4.45}, & k_{s,2}(\text{tr.}) &= 10^{-7.94} \\
 k_{s,1}(\text{gr.}) &= 10^{-5.80}, & k_{s,2}(\text{gr.}) &= 10^{-8.10} \\
 q_0 &= 58, & q_1 &= 1.42, & q_2 &= 0.80
 \end{aligned}$$

From the dissociation constants it is seen that the trans-diaquo ion is an acid about 40 times stronger than the cis-diaquo ion with regard to the dissociation of the first hydrogen ion, but not essentially stronger with regard to the dissociation of the 2nd hydrogen ion. Further the q -values show that the equilibrium in acid solution is strongly displaced in favour of the cis ion, *i.e.* in acid solutions of diaquo salt less than 2 per cent is to be found as trans ion, while neutral and basic solutions contain about equal amounts of cis and trans complex in equilibrium.

The rates of isomerization of the diaquo ions in acid solution and of the dihydroxo ions in basic solution are of the same order of magnitude, but strongly dependent on the purity of salts; with ordinary purified preparations equilibrium is usually reached in about a week. The rates of isomerization of the aquohydroxo ions are much higher⁵ and equilibrium, even with the most thoroughly purified salts, is reached within one hour. It was, therefore, necessary, when determining the cis and trans acidic dissociation constants, to work quickly and to extrapolate the potentials measured to the time zero.

Some preliminary kinetic experiments on the isomerization of trans diaquo salt in acid solution (see Table 3) showed that the reaction was of 1st order,

and almost independent of pH and salt concentration. Addition of small amounts of charcoal increased the reaction velocity many times, and it is, therefore, beyond any doubt that the cis-trans isomerization is partly an heterogenously catalyzed reaction. Charcoal also has a strongly catalyzing effect on the cis-trans isomerization in basic solution, but here, though more slowly, it also brings about an exchange of ligands ^{1, p. 220}. In this way using charcoal as a catalyst, it was possible to determine the 1st hydrolysis constant of the luteo ion ($k_{h,1}$), and our thanks are due to Mr. Flemming Woldbye, who has performed all the experimental work in connection with the estimation of this constant.

Comparison with other systems

Lewis *et al.*⁶ have found that the exchange of radioactive ⁶⁰Co between cobalt(II)-ammonia solutions and the hexamine-cobalt(III) complex is much slower than the exchange between cobalt(II)-ethylenediamine solutions and the tris(ethylenediamine)cobalt(III) complex. This is a simple question of electron transfer, and it is not at variance with the fact that the cobalt(III) complexes with ethylenediamine have by far the greatest robustness.

ter Horst⁷ has shown qualitatively that the trans-diaquotetrammine-cobalt(III) ion is a stronger acid than the corresponding cis compound. The adjustment of the cis-trans equilibrium is here more rapid than for the analogous ethylenediamine complexes, and the acidic dissociation constants for the diaquotetrammine-cobalt(III) ion determined by Lamb and Damon⁸, $k_{s,1} = 10^{-5.32}$ and $k_{s,2} = 10^{-7.30}$ ($\mu = 0.02$, 25° C), are, therefore, undoubtedly gross dissociation constants. J. Bjerrum's calculation of k_5 in the cobalt(III)-ammonia system ^{1, p. 284} must consequently be correct.

That the trans-diaquo ion is a stronger acid than the cis-diaquo ion is also true for the diaquodiammine-platinum(II) ions⁹.

The cause of such a "trans" effect was first discussed by Grünberg¹⁰, who tried to explain it on a purely electrostatic basis. Some calculations made in Table 1 seem to show that the effect only appears in complexes with typical covalent bonds. The data compiled are computed on the following basis:

In an octahedral system where β_1 denotes the Ostwald factor by which the ethylenediamine molecule first bound to the metal ion lowers the tendency to take up a 2nd molecule in the "planar position", and analogously β_2 denotes the corresponding factor for the uptake in the "angle position", the ratio of the consecutive formation constants is given by

$$\frac{k_1}{k_2} = \frac{24}{5} \cdot \frac{5\beta_1}{4\beta_1 + \beta_2} \cdot \beta_2, \quad \frac{k_2}{k_3} = \frac{75}{8} \cdot \frac{(4\beta_1 + \beta_2)^2}{25\beta_1^2} \cdot \beta_2, \quad q_0 = \frac{4\beta_1}{\beta_2} \quad (7)$$

Table 1. Equilibrium constants and Ostwald factors in some ethylenediamine systems.
 $\mu = 1$, 30° C.

		$\log k_1$	$\log k_2$	$\log k_3$	$\log K_3$	q_0	β_1	β_2
Mn ⁺⁺	+ 3 en	2.73	2.06	0.88	5.66	(2.1)	0.60	1.15
Fe ⁺⁺	+ 3 en	4.28	3.25	1.99	9.52	(5.2)	2.76	2.14
Co ⁺⁺	+ 3 en	5.89	4.83	3.10	13.82	(1.5)	1.15	3.16
Ni ⁺⁺	+ 3 en	7.66	6.40	4.55	18.61	(1.7)	2.08	4.78
Co ⁺⁺⁺	+ 3 en	(18.7)	(16.2)	13.81	48.69	58	632	43.5

The formulae (7) are obtained by J. Bjerrum^{1, p. 95} using the assumption that the factor by which the ethylenediamine molecules in an angle position to each other resist the uptake of the 3rd ethylenediamine molecule, is equal to the product of the action of the individual ligands — or, in this particular instance, β_2^2 . It follows directly from the formulae that the ratio between the consecutive constants may be regarded as a product of the statistical factor (24/5 and 75/8 respectively), the β_2 -factor and an asymmetry factor which vanishes when $\beta_1 = \beta_2$. In this special case we have for the cis-trans constant of the diaquo ions $q_0 = 4$.

In the systems of divalent iron group metal ions the values for q_0 given in parenthesis and the Ostwald factors β_1 and β_2 are estimated from the previously^{1, p. 217} determined consecutive formation constants in 1 N KCl at 30° by means of formulae (7). In the cobalt(III)-ethylenediamine system the gross complexity constant $K_3 = k_1 k_2 k_3$ has previously been determined in 1 N salt solution at 30°^{1, p. 233} by combination of the normal potentials of the aquo ions and the tris(ethylenediamine) ions with the corresponding value for K_3 in the cobalt(II) system. Of the values found in this paper the cis-trans constant ($q_0 = 58$) has probably the same value at 25° and 30° (cf. p. 1278), and the 3rd formation constant ($k_3(\text{gr.}) = 10^{13.99}$ in 1 N NaNO₃ at 25°) has been converted to 30° using some thermochemical data of Yatsimirskii¹¹. The estimated values for the 1st and 2nd formation constants given in parenthesis in Table 1, as well as the β -factors have been computed on this basis, and it will be seen that it is especially the β_1 -factor for planar uptake of the 2nd ethylenediamine that has an extraordinarily high value.

EXPERIMENTAL

Preparation of salts. With minor modifications the complex salts used were prepared according to methods described in the literature. Tris(ethylenediamine)cobalt(III) nitrate was made in excellent yield from cobalt(II) nitrate and aqueous ethylenediamine using decolorizing charcoal as a catalyst^{1, 2}. *Anal.* Calc. for Co en₃(NO₃)₃ : Co 13.86,

N 29.65. Found: Co 13.89, N 29.89. It was shown that further recrystallization from water had no demonstrable influence on the absorption spectrum of the salt in aqueous solution.

Cis-diaquobis(ethylenediamine)cobalt(III) nitrate was prepared from the corresponding bromide¹², which again was prepared from Werner's brown nitrate¹³. The oxidation of cobalt(II) nitrate to brown salt was made in photographic trays over which a stream of air was blown from a ventilator. In this way the time of preparation was reduced from days to hours. The crude product was recrystallized once and dried at 60°. *Anal.* Calc. for $[\text{Co}(\text{Co}(\text{OH})_2\text{en}_2)_3](\text{NO}_3)_6$: N 23.34. Found: N 23.15.

During the further treatment of brown nitrate with 10 N HBr a stream of air was blown over the reaction mixture and not more than 5 g were treated in every run as it is difficult with greater portions to remove the bromine formed during the reaction quickly enough to get a good yield. In order to convert to the nitrate, the freshly prepared bromide was dissolved in dilute nitric acid at -5° , aerated to remove bromine, and precipitated with the double volume of alcohol. The salt was reprecipitated using the same procedure and dehydrated over CaCl_2 . *Anal.* Calc. for $[\text{Co en}_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$: Co 14.69. Found: Co 14.61. Further reprecipitation using the same procedure had no influence on the absorption spectrum, and the salt could be kept unchanged for months in a bottle with a tight fitting stopper.

Trans-diaquobis(ethylenediamine)cobalt(III) nitrate was prepared directly from the trans-dihalogeno salts $[\text{Co en}_2 \text{Br}_2] \text{Br}$ or $[\text{Co en}_2 \text{Cl}_2] \text{Cl}$. The halogeno salts were treated in portions of 2 g at 0°C with the equivalent amounts of Ag_2O and about twice the equivalent amounts of water. In the case of the chloride it was necessary to start the reaction before cooling the mixture. The solutions were quickly filtered from the silver halogenide and at -10°C twice the calculated amount of fuming nitric acid was added and the solution slowly precipitated with icecold alcohol. The trans-salt was easily freed from the more soluble cis-salt by reprecipitation with alcohol in presence of nitric acid. It was purified until the spectrum was unchanged by further reprecipitation. *Anal.* Calc. for $[\text{Co en}_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$: Co 14.69. Found: Co 14.70.

Analytical methods. Cobalt was determined after complete decomposition of the complexes with concentrated sulphuric acid. In the later experiments the decomposition was made and excess of H_2SO_4 conveniently removed by heating on an infrabath. In analysis of pure complex salts and of solutions also containing other metal salts, different methods were used. In the first case cobalt was determined by weighing as CoSO_4 after heating in an electric furnace at 550°C , and in the second case according to Yardley¹⁴, by potentiometric titration of the cobalt(II)-citrate complex in ammoniacal solution with ferricyanide in an atmosphere of oxygenfree nitrogen Cf. 1, p. 266 ff.

In the sulphuric acid destruction of the cobalt(III) complexes ethylenediamine is partly oxidized to N_2 . For this reason nitrogen in the solid complex salts was determined by the Dumas method, and a potentiometric method worked out for the determination of free ethylenediamine in alkaline solutions of the cobalt(III) complexes (see p. 1281).

Solutions. The different solutions were prepared in calibrated measuring flasks by weighing the pure complex salts and by weighing or pipetting from stock solutions of sodium nitrate, nitric acid, and ethylenediamine as previously described¹⁵, p. 12. Carbon dioxide-free sodium hydroxide solutions were prepared according to the Sørensen method.

ACID-BASE CONSTANTS OF THE SYSTEM OF DIAQUO IONS

The acid-base constants of the system of diaquobis(ethylenediamine) ions were determined by means of glass electrode measurements in solutions of the complex salts to which suitable amounts of sodium hydroxide had been added. The data are given in Table 2. The composition of the solutions is given in terms of the total concentrations of cobalt(C_{Co}) and of sodium hydroxide (C_{NaOH}). The cobalt concentrations are denoted by cis and trans, respectively, as well as by gr. for solutions in equilibrium with respect to cis and trans. The true hydrogen ion concentration $[H^+]$ was determined in all cases by standardizing against a standard acid solution of the composition: $C_{HNO_3} = 0.00499$, $C_{NaNO_3} = 1.000$. The measurements were performed in an electrically heated air thermostat with a "Radiometer" valve potentiometer, Model PHM 3.

Due to the great velocity with which the isomerization of the diaquo salts occurs in the buffer range, it was necessary to work very quickly in order to obtain the acidic dissociation constants for the pure isomers. An experiment was started by the addition from a Krogh syringe pipette of the proper amount of titrated sodium hydroxide to a freshly made and suitably diluted solution of the cobalt salt. In this way it was possible to take the first reading about 30 seconds after the addition of the base.

A typical example is the following: 0.997 ml 0.1072 *N* NaOH was added to 19 ml of a solution containing 4.00 ml 5 *N* $NaNO_3$ and 0.08734 g trans-nitrate, total volume corrected 20.03 ml (sol. no. 4 in Table 2), and the following potentials were obtained at the times mentioned:

extrapol.							
<i>t</i> (sec.)	0	40	70	100	130	160	∞
<i>E</i> (volt)	-0.1410	-0.1420	-0.1428	-0.1438	-0.1445	-0.1455	-0.2201

In the extrapolated potential E ($t = 0$) is a little uncertainty due to the time it takes for the glass electrode to adjust itself, but this uncertainty scarcely amounts to more than 0.5 mV. In the example given E_{st} , the potential of the standard acid solution with $[H^+] = 0.00499$, had the value -0.0138 at the time $t = 0$, and two hours later the value -0.0140 , at the time when the equilibrium potential E ($t = \infty$) was measured.

The average number of protons produced by the diaquo ion is given by

$$\bar{p} = \frac{C_{NaOH} + [H^+] - [OH^-]}{C_{Co}}$$

Table 2. The acidic dissociation constants of the diaquo-bis(ethylenediamine)cobalt(III) ions in 1 N sodium nitrate solution at 25°.

$$C_{\text{NaNO}_3} = 1.000, \quad -\log[\text{H}^+]_{\text{st.}} = 2.312$$

a. The first dissociation constant.								
No.	$C_{\text{Co}}(\text{cis})$	C_{NaOH}	$\bar{\nu}$	$E_{\text{st.}} - E$	$-\log[\text{H}^+]$	$\log \frac{1-\bar{\nu}}{\bar{\nu}}$	$\log(1+\Delta)$	$-\log k_{s,1}$
1	0.01084	0.005337	0.4923	0.2210	6.051	0.013	0.009	6.074
2	0.01066	0.005337	0.5006	0.2199	6.033	-0.001	0.009	6.041
3	0.01059	0.005337	0.5040	0.2221	6.071	-0.007	0.009	6.073
	$C_{\text{Co}}(\text{tr.})$						$-\log k_{s,1}(\text{cis}):$	6.06
4	0.01086	0.005337	0.4945	0.1272	4.464	0.010	0	4.474
5	0.01046	0.005337	0.5136	0.1273	4.461	-0.023	0	4.438
6	0.01040	0.005337	0.5164	0.1278	4.470	-0.028	0	4.442
	$C_{\text{Co}}(\text{gr.})^*$						$-\log k_{s,1}(\text{tr.}):$	4.45
7	0.009968	0.003969	0.3982	0.1956	5.622	0.179	0.004	5.805
4	0.01086	0.005337	0.4913	0.2061	5.799	0.015	0.006	5.820
5	0.01046	0.005337	0.5103	0.2063	5.803	-0.018	0.006	5.791
8	0.02050	0.01024	0.5110	0.2076	5.825	-0.020	0.007	5.812
9	0.01040	0.006217	0.5978	0.2148	5.948	-0.172	0.011	5.787
10	0.01017	0.006947	0.6831	0.2251	6.114	-0.334	0.014	5.800
							$-\log k_{s,1}(\text{gr.}):$	5.80
b. The second dissociation constant.								
No.	$C_{\text{Co}}(\text{cis})$	C_{NaOH}	$\bar{\nu}$	$E_{\text{st.}} - E$	$-\log[\text{H}^+]$	$\log \frac{2-\bar{\nu}}{\bar{\nu}-1}$	$-\log(1+\Delta)$	$-\log k_{s,2}$
11	0.01493	0.02150	1.440	0.3429	8.113	0.095	-0.013	8.194
12	0.01453	0.02150	1.479	0.3461	8.168	0.036	-0.010	8.195
13	0.01419	0.02150	1.515	0.3490	8.217	-0.026	-0.008	8.183
	$C_{\text{Co}}(\text{tr.})$						$-\log k_{s,2}(\text{cis}):$	8.19
14	0.01516	0.02150	1.418	0.3237	7.788	0.144	0	7.932
15	0.01424	0.02150	1.510	0.3340	7.963	-0.017	0	7.946
16	0.01404	0.02150	1.531	0.3360	7.997	-0.054	0	7.943
	$C_{\text{Co}}(\text{gr.})^*$						$-\log k_{s,2}(\text{tr.}):$	7.94
17	0.009816	0.01343	1.368	0.3280	7.862	0.246	-0.014	8.094
14	0.01516	0.02150	1.418	0.3340	7.963	0.144	-0.010	8.097
18	0.01013	0.01488	1.473	0.3397	8.060	0.047	-0.007	8.100
19	0.01682	0.02482	1.475	0.3403	8.071	0.043	-0.007	8.107
20	0.01418	0.02150	1.527	0.3462	8.170	-0.047	-0.005	8.118
21	0.01347	0.02150	1.596	0.3510	8.251	-0.169	-0.004	8.078
22	0.01026	0.02150	1.623	0.3555	8.326	-0.218	0	8.108
							$-\log k_{s,2}(\text{gr.}):$	8.10

* Nos. 7, 8, 9, 10, 17, 18, 19, 21 are prepared from cis-salt, nos. 4, 5, 14, 20, 22 from trans-salt.

and connected with the acidic dissociation constants through the expression:

$$\bar{\nu} = \frac{k_{s,1}[\text{H}^+] + 2 k_{s,1} \cdot k_{s,2}}{[\text{H}^+]^2 + k_{s,1}[\text{H}^+] + k_{s,1} \cdot k_{s,2}}$$

When this equation is solved with respect to $k_{s,1}$ and $k_{s,2}$ and arranged in the proper way ^{cf. 16, p. 13}, we get the following expressions for the two constants for $\bar{\nu} < 1$ and $\bar{\nu} > 1$, respectively:

$$-\log k_{s,1} = -\log[\text{H}^+] + \log \frac{1-\bar{\nu}}{\bar{\nu}} + \log \left(1 + \frac{(2-\bar{\nu}) k_{s,2}}{(1-\bar{\nu})[\text{H}^+]} \right)$$

$$-\log k_{s,2} = -\log[\text{H}^+] + \log \frac{2-\bar{\nu}}{\bar{\nu}-1} - \log \left(1 + \frac{\bar{\nu}[\text{H}^+]}{(\bar{\nu}-1)k_{s,1}} \right)$$

The reciprocal influence of $k_{s,1}$ and $k_{s,2}$ finds its expression in the last terms, which are negligibly small in the trans system and in the other cases only give a minor correction. $\bar{\nu}$ is varied to some extent in the equilibrium solutions, but is kept close to 0.5 and 1.5, respectively, in the solutions of the unstable isomers in order to obtain the smallest possible uncertainty in the estimated constants. Table 2 gives, besides the constants found and their mean values, the values of the individual terms in the calculation.

SPECTROPHOTOMETRIC INVESTIGATION OF THE SYSTEM OF DIAQUO IONS

In Fig. 1 are given extinction curves for tris- and bis(ethylenediamine) cobalt(III) complexes in 1 *N* NaNO₃. The molar extinction coefficient

$$\epsilon = \frac{\log_{10} I_0/I}{C_{\text{Co}} \cdot d}$$

(I_0 and I denote the intensity of the incident and the transmitted light, respectively, and d the thickness of the absorbing layer in cm) is plotted as ordinate, and the wave number in cm^{-1} as abscissa; for orientation purposes the wavelength in $\text{m}\mu$ is also plotted. Cobalt(III) complexes have practically no light absorption above 700 $\text{m}\mu$, and below 350 $\text{m}\mu$ the nitrate ion begins to absorb ($\epsilon_{350} = 0.018$), and for this reason the extinction coefficients are examined in the range 350–700 $\text{m}\mu$ only. For the diaquo and dihydroxo ions the extinction coefficient is denoted by ϵ_0 and ϵ_2 , respectively, in accordance with the designations of the q -constants in formulae (4). The effect of the sodium nitrate medium on the spectra is negligibly small, and as a whole the extinction coefficients of the complexes are only 1–2 % higher in 1 *N*

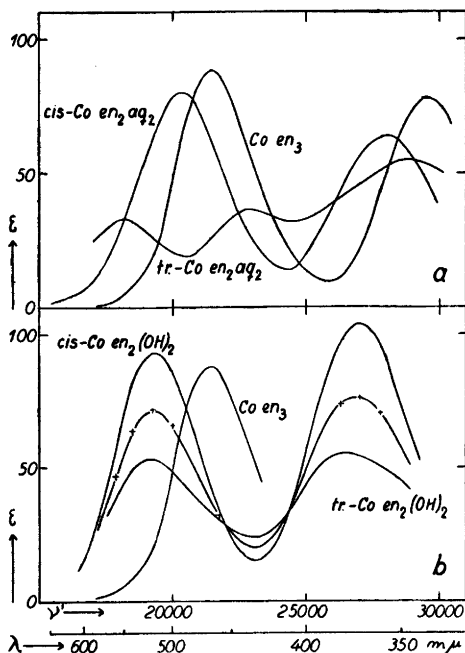


Fig. 1. Extinction curves for tris- and bis(ethylenediamine)cobalt(III) complexes in 1 N NaNO₃. — ϵ = the molar extinction coefficient, ν' the wave number in cm^{-1} , and λ the wavelength in $\text{m}\mu$. a: Curves for luteo, cis and trans diaquo ions. b: Curves for luteo, cis and trans, and the equilibrium of isomeric dihydroxo ions. The equilibrium curve of cis and trans dihydroxo ions is calculated from the spectra of the pure isomers by means of the average value found for the cis-trans constant: $q_2 = 0.80$. The + points mark the experimental mean values for $\epsilon_2(\infty)$ in Table 4a.

NaNO₃ than in water. The extinctions were measured at $23 \pm 1^\circ \text{C}$. A Beckman DU spectrophotometer with ordinary equipment was used for the measurements.

Cis-trans isomerizations. The velocity with which trans-diaquo salt changes into cis salt was examined at $492 \text{ m}\mu$, a wavelength which is especially suited for an investigation of this kind (see Fig. 1a). The acidic solutions of the diaquo salt were placed (or in the experiments with added charcoal shaken) in a water thermostat at 25°C , and at proper intervals of time samples were taken for optical analysis. The data are given in Table 3. The constancy of $\frac{-\log(1-\alpha)}{\text{time}}$ (α = degree of reaction) shows that the isomerization is approximately a 1st order reaction in the experiments both with and without added charcoal. $t_{1/2}$ gives the times of half-completion. The end values for the extinction as determined in experiment 3 and 4 are seen to correspond very nearly to complete conversion into cis salt: $\epsilon_0 = 80.9 \left(\frac{0.786}{C_{\text{Co}}} = 81.0 \right.$ in exp. 3 and $\frac{0.655}{C_{\text{Co}}} = 81.4$ in exp. 4, respectively). The experiments mentioned were made with our purest preparation of trans-diaquo salt and were reproducible as long as the same preparation was used.

Table 3. Isomerization velocity of *trans*-diaquobis(ethylenediamine)cobalt(III) nitrate in acidic solution at 25°.

Wavelength 492 m μ : Mean extinction coefficients used
 $\epsilon_0(\text{tr.}) = 19.2$, $\epsilon_0(\text{cis}) = 80.9$ ($C_{\text{NaNO}_3} = 1$), 80.0 (dilute)

Exp.	C_{NaNO_3}	C_{HNO_3}	C_{Co}	$\frac{\text{g Norite}}{100 \text{ ml}}$	t (min.)	$\frac{\log \frac{I_0}{I}}{d}$	$\frac{-\log(1-\alpha)}{t}$	$t_{1/2}$ (min.)
1	0	0.05	0.00989	0	2	0.191		
					56	0.216	0.000322	
					118	0.239	0.000305	
					177	0.264	0.000316	
					239	0.291	0.000330	
					298	0.316	0.000339	
					1383	0.587	0.000338	
					Mean		0.000325	926
2	0	0.10	0.01002	0	3	0.192		
					119	0.239	0.000302	
					183	0.260	0.000284	
					243	0.286	0.000300	
					299	0.303	0.000294	
					344	0.318	0.000294	
					Mean		0.000295	1020
3	1.00	0.05	0.00970	0	3	0.187		
					193	0.296	0.000456	
					243	0.325	0.000470	
					297	0.354	0.000480	
					356	0.386	0.000494	
					3236	0.786		
Mean		0.000473	637					
4	1.00	0.05	0.008046	0.040	75	0.428	0.00467	
					132	0.550	0.00525	
					205	0.610	0.00533	
					1565	0.655		
					Mean		0.0051	59

In alkaline solution it is possible to follow the transformation of *cis*- as well as of *trans*-dihydroxo ion to a state of equilibrium. A selection of the measurements made is given in Table 4. In part *a* of the table the isomerization is followed directly by measuring the extinction coefficients of the alkaline solutions at various times, and in part *b* by transforming dihydroxo ions to diaquo ions before measuring the extinction coefficients. In connection with

the neutralization and acidification, the volume was doubled and enough sodium nitrate added to obtain a 1 *N* solution of the salt in question.

The tables give mean values for the extinction coefficients of the pure isomers as well as for the equilibrium mixtures at various wavelengths. Complete isomerization is reached after about 7 days at 25° C and after further standing for 589 days the equilibrium spectrum is practically unchanged. The equilibrium spectra at 25° C as well as the spectra of solutions on the way towards equilibrium are within the uncertainty of the measurements composed of only 2 components. The common points of intersection (see also Fig. 1) as well as the independence of wavelength of the computed values for the degrees of reaction of cis salt

$$\alpha_{\text{cis}} = \frac{\epsilon_2(\text{cis}) - \epsilon_2(\text{time})}{\epsilon_2(\text{cis}) - \epsilon_2(\text{tr.})}, \text{ or } \frac{\epsilon_0(\text{cis}) - \epsilon_0(\text{time})}{\epsilon_0(\text{cis}) - \epsilon_0(\text{tr.})}$$

and of trans salt ($\alpha_{\text{tr.}}$), respectively, give clear evidence of this. The cis-trans constant q_2 is calculated from the extinction coefficients corresponding to equilibrium $\epsilon_2(\infty)$, or $\epsilon_0(\infty\epsilon_2)$, and the extinction coefficients of the pure isomers, by the expressions

$$q_2 = \frac{[\text{cis}]}{[\text{tr.}]} = \frac{\epsilon_2(\infty) - \epsilon_2(\text{tr.})}{\epsilon_2(\text{cis}) - \epsilon_2(\infty)}, \text{ or } \frac{\epsilon_0(\infty\epsilon_2) - \epsilon_0(\text{tr.})}{\epsilon_0(\text{cis}) - \epsilon_0(\infty\epsilon_2)}$$

The uncertainty of the estimated values of q_2 is approximately proportional to the differences of extinction coefficients $\epsilon_2(\text{cis}) - \epsilon_2(\text{tr.})$, or $\epsilon_0(\text{cis}) - \epsilon_0(\text{tr.})$, of the pure isomers at the wavelength in question. For this reason rounded off values of the extinction coefficient differences mentioned were used as weights in the calculation of the mean values for q_2 as well as for the degrees of reaction given in the last column of Tables 4. The average value, $q_2 = 0.81$, found at 25° C in weaker alkaline solution (Table 4a: $C_{\text{NaOH}} = 0.027 - 0.24$) is seen to be in satisfactory agreement with the average value, $q_2 = 0.79$, at 25° C in Table 4b ($C_{\text{NaOH}} = 0.50$), and the average of these 2 values, $q_2 = 0.80$, has been taken as the final mean value for the cis-trans constant in alkaline solution.

The estimated values for the degrees of reaction given in Tables 4 give some information about the kinetics of the isomerization. The 1st order rate constant for the transformation of cis into trans is given by the expression

$$k_{\text{rate}} = \frac{-\log(1 - \alpha_{\text{cis}}(1 + q_2))}{\text{time} \cdot (1 + q_2)}$$

and the time of half-completion by

$$t_{1/2} = \frac{\text{time} \cdot \log 2}{-\log(1 - \alpha_{\text{cis}}(1 + q_2))}$$

Table 4. *Cis-trans equilibria of the dihydroxobis(ethylenediamine)cobalt(III) ions.*

a. Extinction coefficients measured directly in the alkaline solution.

			$C_{\text{Co}} \sim 0.01, C_{\text{NaNO}_2} = 1.00$									
No.	time at t °C		C_{NaOH}	360	370	380	460	500	520	540	560 $m\mu$	Av.
$\epsilon_2(\text{cis})$, av.	1-4	0	0.03-0.10	95.5	103.6	97.5	33.3	85.5	93.0	82.1	55.4	
$\epsilon_2(\text{tr.})$, av.	5	0	0.0268	50.5	53.9	54.9	30.5	48.1	53.0	49.3	38.6	
$\epsilon_2(\text{cis}) - \epsilon_2(\text{tr.})$				45.0	49.7	42.6		37.4	40.0	32.8	16.8	
Cis salt	3	2 days at 25°	0.0268	77.0	83.3	79.4	32.3	69.8	75.8	66.6	47.5	
α_{cis} (2 days)				0.412	0.408	0.425		0.420	0.430	0.472	0.470	0.427
Cis salt	»	4 » » »	»	73.2	78.5	76.1	32.3	66.7	72.7	63.9	46.7	
» »	»	7 » » »	»	71.1	76.4	74.2	31.8	65.7	71.4	63.7	46.9	
» »	»	19 » » »	»	71.4	76.5	74.2	31.9	65.8	72.5	64.7	47.3	
» »	»	4 47 » » »	0.0970	69.0	74.9	73.1	—	65.3	71.2	63.6	—	
» »	»	589 » » »	»	71.0	77.0	75.0	31.8	65.0	70.5	63.2	46.5	
» »	»	6 13 » » »	0.2422	70.1	—	74.2	—	65.1	71.0	63.0	46.6	
Trans salt	5	2 » » »	0.0268	64.1	69.5	68.1	32.2	60.0	65.0	58.9	43.3	
α_{tr} (2 days)				0.302	0.314	0.310		0.318	0.300	0.293	0.280	0.305
Trans salt	»	4 » » »	»	67.7	73.1	71.5	32.4	63.5	68.9	61.2	45.0	
» »	»	7 » » »	»	69.5	75.0	72.9	32.4	65.7	71.0	63.4	47.0	
$\epsilon_2(\text{Co})$, av.	3-6			70.2	75.7	73.7	32.0	65.5	71.4	63.7	46.8	
q_2 (25°)				0.78	0.78	0.79		0.87	0.85	0.78	0.95	0.81
Cis salt	7	5 min. at 80°	0.0254	76.0	79.7	76.6	—	63.7	69.2	62.5	46.3	
» »	»	15 » » »	»	75.9	79.7	76.9	—	—	69.3	62.4	46.2	
» »	»	105 » » »	»	74.9	79.4	76.9	33.4	64.0	69.1	62.9	46.6	
q_2 (80°)				(1.18)	(1.05)	(1.07)		0.74	0.67	0.71	0.91	0.72

b. Extinction coefficients measured shortly after neutralization with nitric acid.

Concentrations in the alkaline solution: $C_{\text{Co}} \sim 0.02, C_{\text{NaNO}_2} = 1 - C_{\text{NaOH}}$ and after acidifying etc.: $C_{\text{HNO}_2} \sim 0.05, C_{\text{Co}} \sim 0.01, C_{\text{NaNO}_2} = 1.00$.

No.	time at t °C		C_{HNO_2}	370	380	410	444	480	492	520	550 $m\mu$	Av.
$\epsilon_0(\text{cis})$, av.	8-11	0	0.01	57.0	44.2	14.3	33.2	76.2	80.9	62.7	32.8	
$\epsilon_0(\text{tr.})$, av.	12-15	0	0.05	46.0	40.9	32.0	35.1	20.0	19.2	26.2	32.8	
$\epsilon_0(\text{cis}) - \epsilon_0(\text{tr.})$				11.0		-17.7		56.2	61.7	36.5		
			C_{NaOH}									
Cis salt	16	368 min. at 25°	0.503	55.5	43.5	15.0	—	71.4	75.8	59.6	—	
α_{cis} (368 min.)				0.136		0.040		0.085	0.083	0.085		0.085
Cis salt	»	26½ hours » »	»	53.1	42.8	18.8	—	60.1	63.1	—	—	
α_{cis} (26½ hours)				0.355		0.254		0.287	0.288			0.290
Cis salt	»	50 » » »	»	52.0	42.7	21.3	—	53.1	55.3	—	—	
α_{cis} (50 hours)				0.454		0.395		0.411	0.415			0.415
Cis salt	»	42 days » »	»	—	42.9	24.1	—	46.5	47.9	42.9	—	
» »	17	7 » » »	0.504	51.5	44.0	24.5	34.4	44.1	46.4	42.1	—	
» »	»	17 » » »	»	52.2	43.6	25.1	34.8	45.0	46.2	42.3	32.6	
Trans salt	18	7 » » »	»	50.6	42.3	24.4	34.2	44.2	45.6	41.2	31.8	
» »	»	17 » » »	»	50.6	42.3	24.2	34.1	44.8	46.1	42.1	32.5	
$\epsilon_0(\text{Co}\epsilon_2)$, av.	16-18			51.2	43.0	24.5	34.4	44.9	46.4	42.1	32.3	
q_2 (25°)				0.90		0.74		0.80	0.79	0.77		0.79
Cis salt	19	c. 1 min. at 100°	0.050	—	45.1	26.4	35.0	44.5	46.0	41.0	32.3	
q_2 (100°)						(0.46)		0.77	0.77	0.68		0.75

By inserting the data for sol. 16, Table 4b, in these formulae we get

C_{NaOH}	t (min.)	$\alpha_{\text{cis}}(\text{av.})$	$\frac{-\log(1-1.8\alpha_{\text{cis}})}{1.8 \cdot t}$	$t_{1/2}(\text{min.})$
0.503	368	0.085	0.000109	1539
»	1590	0.290	0.000112	1496
»	3000	0.415	0.000111	1512

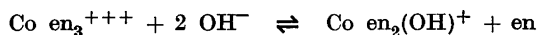
The time of half-completion is seen to be longer than for the isomerization in acidic solution, but it must be mentioned that one of the authors (J. Bjerrum) has once investigated a cis salt with a several times longer time of half-completion than the salt examined here. The average values for α_{cis} and α_{tr} after two days (sols. 3 and 5, Table 4a) satisfy the equation $q_2 = \frac{\alpha_{\text{tr}}}{\alpha_{\text{cis}}}$, fairly well, but this should be considered as a simple coincidence, which shows that the two salts in question are of the same purity and therefore also heterogeneously catalyzed to about the same extent.

At temperatures above 80° C the cis-trans equilibrium is established in a few minutes as shown by sols. 7 and 19 in Tables 4. The extinction coefficients for the cis-trans equilibrium are too high in the near ultraviolet (probably due to small amounts of ultraviolet absorbing by-products) — and after prolonged heating the solutions became visibly opaque. The values for q_2 estimated from the ultraviolet extinction coefficients in basic solution are too high for this reason, and conversely the value estimated at 410 m μ from the extinction coefficients in acidic solution is too low (see Fig. 1). But the average values for visible light show clearly that the influence of temperature on q_2 is very small.

q_2 can also be calculated alone from the acidic dissociation constants of the systems of diaquo ions. From the formulae (6) this can be done in 2 ways giving $q_2 = 0.66$ and 1.34, respectively. These values are much more uncertain than the direct spectrophotometrically determined value, $q_2 = 0.80$, and the best values for q_0 and q_1 are obtained by combining the last mentioned value for q_2 with the expressions which contain only products of the mass action constants. Thus we get $q_0 = 58$, and $q_1 = 1.42$ (cf. p. 1267).

THE HYDROLYSIS CONSTANT ($k_{h,1}$) OF THE TRIS(ETHYLENEDIAMINE)-COBALT(III) COMPLEX (IN COLLABORATION WITH FLEMMING WOLDBYE)

In alkaline solution charcoal catalyzes the hydrolysis equilibrium of the tris(ethylenediamine)cobalt(III) ion:



but the introductory experiments showed that the equilibrium adjustment takes place with much more difficulty than in the corresponding cobalt(III) ammonia system. The charcoal acts as a catalyst only for a short time after its addition though at the same time it decomposes the complexes to some extent, whereupon its catalytic effect comes almost to a stop. As a consequence of this, equilibrium could be obtained only by adding the charcoal in small portions until further addition caused no change in the calculated hydrolysis constant.

The same kind of "Norite" charcoal was used in all experiments. In every experiment 200 ml of the initial solution, the composition of which is given in Table 5a, were shaken with the charcoal in 250 ml flasks (kept tightly closed by a rubber cover over the glass stopper) in a water thermostat at 25.0° C. Table 5b gives the amounts of charcoal added during the equilibrium adjustment, and the times (in hours) the solutions have been shaken since the first addition of charcoal. Usually when portions of charcoal were added, samples of the solutions were analyzed spectrophotometrically after being carefully filtered. The extinction curves of tris(ethylenediamine) salt and of the cis-trans equilibrium mixture of dihydroxo ions are given in Fig. 1b. The common point of intersection of the curves $\epsilon_{494} = 61.0$ was used to compute the cobalt concentration

$$C_{\text{Co}}(\text{opt.}) = \frac{\log_{10} I_0/I}{61.0 \cdot d}$$

and the degrees of conversion of luteo salt into dihydroxo salt

$$\alpha_\lambda = \frac{\epsilon_\lambda - \epsilon_{\text{Co en}_3^{+++}}}{\epsilon_2(\infty) - \epsilon_{\text{Co en}_3^{+++}}}$$

were calculated at 560 and 580 $m\mu$ by inserting the following values for the extinction coefficients:

	560	580 $m\mu$
$\epsilon_{\text{Co en}_3^{+++}}$	2.12	1.24
$\epsilon_2(\infty)$	46.8	28.7

The data collected in Table 5b show that α_{560} and α_{580} follow each other very closely, and further that the cobalt concentration C_{Co} (titr.) determined by potentiometric titration (see p. 1270) in the equilibrium solutions agrees well with the optically determined cobalt concentration. This can be taken as a proof that in all the solutions examined we have a mixture of luteo and dihydroxo salt only.

Table 5. Estimation of the hydrolysis constant $k_{h,1}$ in $\sim 1 N NaNO_3$ at 25° .

a. Composition of initial solutions.								
No.	$C_{NaNO_3}^0$	C_{NaOH}^0	C_{en}^0	C_{Co}^0	Co-salt			
1	1.000	0.06655	0.0943	0.01512	Co en ₃ (NO ₃) ₃			
2	1.000	0.1023	0.0979	0.01558	»			
3	1.000	0.1023	0.0616	0.01581	»			
4	1.000	0.1137	0.0965	0.01644	Co en ₂ (H ₂ O) ₂ (NO ₃) ₃			
5	1.000	0.1485	0.0647	0.01658	Co en ₃ (NO ₃) ₃			
6	0.800	0.1930	0.0656	0.02247	Co ₄ en ₆ (OH) ₆ (NO ₃) ₆			
7	0.500	0.5080	0.0636	0.01658	Co en ₃ (NO ₃) ₃			
8	0.250	0.7620	0.0216	0.01525	»			
b. Equilibrium adjustment and optical analysis.								
No.	Hours shaken	g Norite 200 ml	C_{Co} (opt.)	C_{Co} (titr.)	ϵ_{580}	ϵ_{580}	α_{580}	α_{580}
1	0; 16; 24; 41; 48	1; 0.5; 0.5; 0.5; 0.3	0.01034		4.06	2.45	0.0434	0.0430
	65; 85	0.5; 0.3	0.00872		4.22	2.59	0.0470	0.0479
	105		0.00792	0.00793	4.21	2.57	0.0468	0.0472
2	0; 14; 24	0.8; 0; 0	0.01380		4.30	2.64	0.0488	0.0497
	38	0	0.01378		4.80	2.91	0.0600	0.0594
	111	0.6	0.01378		6.12	3.76	0.0895	0.0895
	135	0.6	0.01228		7.00	4.38	0.1092	0.1116
	156		0.01048	0.01053	7.19	4.44	0.1135	0.1138
3	0; 14	1; 0	0.01363		5.16	3.14	0.0680	0.0675
	24	0	0.01358		6.40	4.06	0.0958	0.1001
	38	0	0.01361		6.78	4.16	0.1043	0.1039
	62	0.2	0.01358		7.68	4.75	0.1244	0.1249
	110	0.2	0.01274		8.60	5.36	0.1450	0.1465
	135	0.6	0.01181		9.34	5.91	0.1616	0.1660
	156		0.01017	0.01014	9.27	5.82	0.1600	0.1629
4	0; 14	1; 0.5	0.01486		26.68	16.29	0.550	0.535
	25; 39	0.5; 0.5	0.01225		14.23	9.02	0.2710	0.2761
	63	0.5	0.01122		10.83	6.84	0.1949	0.1989
	80	0.5	0.01042		9.57	5.95	0.1667	0.1673
	116		0.00952	0.00942	9.59	5.98	0.1672	0.1683
5	0; 16; 24; 41; 48	1; 0.5; 0.5; 0.5; 0.3	0.01135		13.91	8.64	0.2639	0.2628
	65; 88; 105	0.5; 0.3; 0.3	0.00892		15.52	9.77	0.3000	0.3029
	108	0.3	0.00818		16.03	10.11	0.3113	0.3153
	128		0.00744	0.00739	15.39	9.59	0.2970	0.2967
6	0; 18; 43; 72	1; 1; 0.5; 0.5	0.01541		30.25	19.09	0.630	0.635
	92		0.01469	0.01496	30.64	19.39	0.638	0.645
7	0; 15; 24; 39	1; 0.5; 0.5; 0.5	0.01282		39.63	25.25	0.840	0.854
	63; 65	0.5; 0	0.01114	0.01122	39.43	24.95	0.835	0.843
8	0; 18; 43; 72; 92	1; 1; 0.5; 0.5	0.01092	0.01100	45.53	28.65	0.972	0.974

Table 5. *continued.*

c. Analysis of equilibrium solutions.

No.	$2C_{\text{en}} + C_{\text{OH}^-} + 1.89aC_{\text{Co}}$	$C_{\text{en}} + 1.79aC_{\text{Co}}$	C_{en} (exp.)	C'_{en} (calc.)	C_{OH^-} (exp.)	C'_{OH^-} (calc.)	$k_{h,1}$ (gr.)
1	0.2240	0.0896	0.0889	0.1163	0.0455	0.0442	2.12
2	0.2740	0.0972	0.0951	0.1142	0.0816	0.0847	1.83
3	0.1946	0.0592	0.0563	0.0802	0.0789	0.0820	1.75
4	0.2468	0.0772	0.0744	0.1027	0.0950	0.0895	1.66
5	0.2005	0.0527	0.0488	0.0945	0.0988	0.1165	2.11
6	0.2553	0.0448	0.0277	0.0640	0.1818	0.1850	1.51
7	0.5686	0.0722	0.0554	0.0891	0.4401	0.4731	1.49
8	0.8024	0.0436	0.0245	0.0451	0.7332	0.7278	1.64
						Mean	1.76

The concentrations of hydroxyl ion and free ethylenediamine in the equilibrium solutions were determined by glass electrode titration with a Radiometer pH meter. Fig. 2 gives graphs of such a titration. At the endpoint of the titration for $E \sim 0.165$ volt, $\text{pH} \sim 4.89$, ethylenediamine is titrated as a diacidic base, and at the inflexion point for $E \sim 0.405$ volt, $\text{pH} \sim 9.04$, as a monoacidic base. In the figure, besides E , $\left| \frac{\Delta V}{\Delta E} \right|$ is plotted against the volume V of added nitric acid. According to Gran's calculations¹⁶ this plot

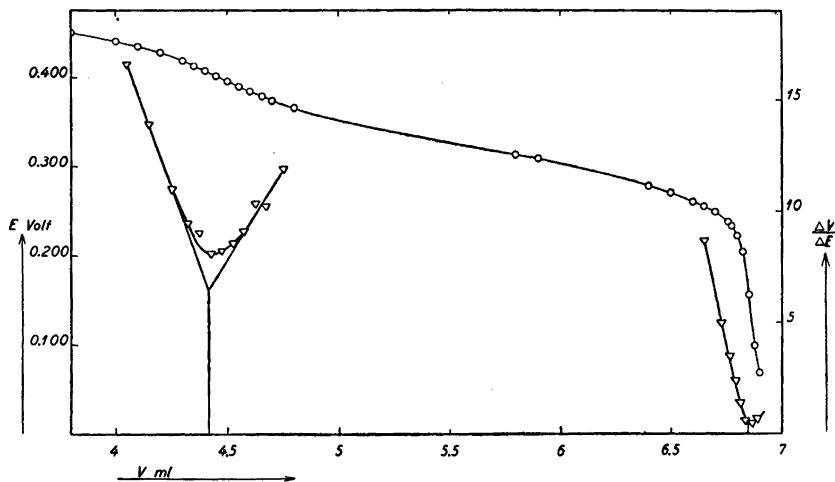


Fig. 2. Potentiometric titration of hydroxyl ion and free ethylenediamine in an equilibrium solution. In the example given 25.00 ml of sol. 2, Table 5, are titrated with 0.999 N HNO_3 , and the o-points give directly the potential E (volt) plotted against the volume V , ml of nitric acid added. The Δ -points give the same titration, but, according to Gran¹⁶, $\left| \frac{\Delta V}{\Delta E} \right|$ is plotted against V .

should transform the curve in the vicinity of the equivalent points into straight lines which intersect each other and the V-axis at the equivalent point. It will be seen that the inflexion points come out much more explicitly in Gran's plot. The reason why the first inflexion point is transformed into a U-shaped curve only, is that the bindings of the 1st and 2nd hydrogen ion to ethylenediamine overlap considerably ($\text{p}k_{\text{enH}_1^{++}} \sim 7.6$ and $\text{p}k_{\text{enH}^+} \sim 10.3$ at room temperature).

The average number of protons taken up by the dihydroxo cobalt(III) ion is at pH: 9.04, $2 - \bar{\nu} = 0.10$ and at pH: 4.89, $2 - \bar{\nu} = 1.89$. For this reason the total amount of acid consumed at the endpoint of the titration corresponds to $2 C_{\text{en}} + C_{\text{OH}^-} + 1.89 \alpha \cdot C_{\text{Co}}$, while the amount of acid consumed between the inflexion point and the endpoint is given by $C_{\text{en}} + 1.79 \alpha \cdot C_{\text{Co}}$. The data are given in Table 5c.

The concentrations of hydroxyl ion and free ethylene diamine were also calculated from the initial concentrations using the assumption that the cobalt lost by every addition of charcoal is absorbed as cobalt(III) hydroxide exclusively ^{cf. 1, p. 262}. This gives the following relations:

$$C'_{\text{en}} = C_{\text{en}} + \Delta C_{\text{en}} = C_{\text{en}}^{\circ} + \alpha \cdot C_{\text{Co}} + 3(C_{\text{Co}}^{\circ} - C_{\text{Co}})$$

$$C'_{\text{OH}^-} = C_{\text{OH}^-} + \Delta C_{\text{OH}^-} = C_{\text{NaOH}}^{\circ} - 2 \alpha \cdot C_{\text{Co}} - 3(C_{\text{Co}}^{\circ} - C_{\text{Co}})$$

when luteo salt is added originally, and similar expressions are easily derived when diaquo salt and brown nitrate are added originally. ΔC_{en} and ΔC_{OH^-} in the formulae indicate the hypothetical concentrations which were removed from the solutions by adsorption of ethylenediamine and hydroxyl ions, respectively. Comparison of the C' -concentrations (see Table 5c) with the directly titrated concentrations seems to show that ethylenediamine is adsorbed to a considerable extent, while the adsorption of hydroxyl ions is smaller and lies within the uncertainty of the computation. This explanation was supported by a few separate adsorption experiments under conditions corresponding to the equilibrium experiments.* In these it was found that the concentration of a 0.1 molar aqueous ethylenediamine was diminished by 13 %, and of a 0.01 molar solution by about 20 %, when shaken with 2 g Norite per 100 ml. In similar experiments with aqueous sodium hydroxide the concentration of a 1 N solution decreased by 1.4 % and of a 0.1 N solution by 4 %, when shaken with 2 g Norite per 100 ml.

* For the making of these measurements the authors are indebted to Miss Lene Rasmussen.

The last column of Table 5c gives the hydrolysis constant $k_{h,1}$ (gr.) calculated from the expression:

$$k_{h,1}(\text{gr.}) = \frac{([\text{cis-Co en}_2(\text{OH})_2^+] + [\text{tr.-Co en}_2(\text{OH})_2^+]) [\text{en}]}{[\text{Co en}_3^{+++}] [\text{OH}^-]^2} = \frac{\alpha \cdot C_{\text{en}}}{(1 - \alpha) C_{\text{OH}^-}^2}$$

where α is taken as the average of α_{560} and α_{580} in the equilibrium solutions. It will be seen that $k_{h,1}$ (gr.) is satisfactorily constant in the whole range examined, where α is varying from 0.04 to 0.97.

The gross hydrolysis constant $k_{h,1}$ (gr.) is connected with the partial cis and trans constants through the equation:

$$k_{h,1}(\text{gr.}) = k_{h,1}(\text{cis}) + k_{h,1}(\text{tr.})$$

Using the mean value found, $k_{h,1}(\text{eq.}) = 1.76$, and combining with the cis-trans constants for the dihydroxo ions, $q_2 = 0.80$, we get:

$$k_{h,1}(\text{cis}) = 0.78, \quad k_{h,1}(\text{tr.}) = 0.98$$

The 3rd formation constants in the cobalt(III)-ethylenediamine system are connected with the hydrolysis constants determined here, the acidic dissociation constants of the diaquo ions, and the ionic concentration product of water $k_{\text{H}_2\text{O}}$ through the expression:

$$k_3 = \frac{k_{h,1} \cdot k_{s,1} \cdot k_{s,2}}{k_{\text{H}_2\text{O}}^2}$$

Inserting in this expression the gross, cis and trans constants of $k_{h,1}$, $k_{s,1}$ and $k_{s,2}$, respectively, and $k_{\text{H}_2\text{O}} = 10^{-13.82}$, *i.e.* the value given by N. Bjerrum and Unmack¹⁷ in 1 *N* KCl at 25°, we get in 1 *N* salt solution:

$$k_3(\text{gr.}) = 10^{13.99}, \quad k_3(\text{cis}) = 10^{13.28}, \quad k_3(\text{tr.}) = 10^{15.24}.$$

SUMMARY

In the extremely inert cobalt(III)-ethylenediamine system it was possible to establish equilibrium in alkaline solutions by a vigorous treatment with charcoal, and the 1st hydrolysis constant of the tris(ethylenediamine) ion could be estimated by analytical methods. In the system of diaquobis(ethylenediamine)cobalt(III) ions the cis-trans equilibria establish themselves spontaneously without exchange of amine molecules, and all acidic dissociation and cis-trans equilibrium constants were determined by glass electrode and spectro-

photometric measurements. In this way not only the 3rd consecutive formation constant, but also the partial formation constants, k_3 (cis) and k_3 (tr.), could be estimated. The data support the idea that Grünberg's "trans" effect appears only in complexes with typical covalent bonds (*vide* Table 1).

REFERENCES

1. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*. (1941). Copenhagen.
2. Bailar, J. C., and Work, J. B. *J. Am. Chem. Soc.* **67** (1945) 176.
3. Uspensky, A., and Tschibisoff, K. *Z. anorg. Chem.* **164** (1927) 326.
4. Uémura, T., and Hirasawa, N. *Bull. Chem. Soc. Japan* **13** (1938) 377.
5. Basolo, F. *J. Am. Chem. Soc.* **72** (1950) 4393.
6. Lewis, W. B., Coryell, C. D., and Irvine, J. W., jr. *J. Chem. Soc.* (1949) (Suppl. Issue no. 2), 386.
7. ter Horst, M. G. *Rec. Trav. Chim.* **54** (1935) 257.
8. Lamb, A. B., and Damon, E. B. *J. Am. Chem. Soc.* **59** (1937) 383.
9. Jensen, K. A. *Z. anorg. Chem.* **242** (1939) 87.
10. Grünberg, A. *Acta Physicochim. (USSR)* **3** (1935) 573.
11. Yatsimirskiĭ, K. B., and Pankova, L. L. *J. Gen. Chem. (USSR)* **19** (1949) 617; Abstr. (1949) 7805.
12. Werner, A., and Jantsch, G. *Ber.* **40** (1907) 268.
13. Werner, A. *Ber.* **40** (1907) 2119.
14. Yardley, J. T. *Analyst* **75** (1950) 156.
15. Bjerrum, J., and Andersen, P. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **22** (1945) no. 7.
16. Gran, G. *Acta Chem. Scand.* **4** (1950) 559.
17. Bjerrum, N., and Unmack, A. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **9** (1929) no. 1.

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