

Studies on Polynuclear Complexes

I. Formation of Polynuclear Hydroxo Complexes in Aged Solutions of Diaquobis(ethylenediamine)cobalt(III) Ions and Kinetics of Decomposition of μ -Dihydroxotetrakis(ethylenediamine)cobalt(III) Ion

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The primary hydrolysis products of the $\text{Co en}_2(\text{H}_2\text{O})_2^{+++}$ ion are the monomeric aquohydroxo and dihydroxo ions. During a slow ageing process polymeric hydrolysis products are formed, but no equilibrium state seems to be obtained even after ageing for years. The rate of the slow hydrolysis is lower in paraffined glass than in ordinary glass vessels. It is shown that μ -hydroxo- and μ -dihydroxo dicobalt ions are not among the hydrolysis products. The tetrakis(ethylenediamine)- μ -dihydroxo ion is found to be decomposed to monomers which react slowly to form new polynuclear ions. The decomposition of this μ -dihydroxo salt is studied in detail, and a mechanism for the decomposition in acidic solution is proposed.

In a previously published paper¹ the system of acid-base and *cis-trans* equilibria of the diaquobis(ethylenediamine)cobalt(III) ions was examined. During our work with this system we noticed that solutions in the buffer range were slowly transformed with an increasing hydrogen ion concentration indicating that polynuclear hydrolysis products were being formed. At the same time changes in the absorption spectrum were observed. For a closer investigation of these phenomena we first carried out a redetermination of the first gross acidic dissociation constant ($K_{s,1}(\text{gr.})$) of *cis-trans* equilibrium mixtures of the diaquobis(ethylenediamine)cobalt(III) ions. Using the same symbols as in Ref.¹, the average number of hydrogen ions produced by the diaquo ions (= number of hydroxyl ions bound per cobalt atom) is given by

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

if $C_{\text{NaOH}} \lesssim 2 C_{\text{Co}}$ and the first gross dissociation constant by

$$-\log K_{s,1}(\text{gr.}) = -\log [\text{H}^+] + \log \frac{1-\bar{\nu}}{\bar{\nu}} + \log (1 + \Delta)$$

when $\Delta = \frac{(2-\bar{\nu}) K_{s,2}(\text{gr.})}{(1-\bar{\nu}) [\text{H}^+]}$.

Table 1. The first gross acidic dissociation constant of the diaquobis (ethylenediamine) cobalt (III) ions in 1 M sodium nitrate at 25° C.

Solutions are made from $\text{cis}[\text{Co en}_2\text{aq}_2](\text{NO}_3)_3$, and all concentrations are given in moles per liter.

$$C_{\text{NaNO}_3} = 1.00 \text{ M}, -\log [\text{H}^+]_{\text{st.}} = 2.297, -\log K_{s,2}(\text{gr.}) = 8.10.$$

C_{Co}	C_{NaOH}	$\bar{\nu}$	$E_{\text{st.}} - E$	$-\log [\text{H}^+]$	$\log \frac{1-\bar{\nu}}{\bar{\nu}}$	$\log (1+\Delta)$	$-\log K_{s,1}(\text{gr.})$
0.01074	0.002708	0.2524	179.6	5.336	0.472	0.002	5.810
0.009936	0.003256	0.3277	189.4	5.502	0.312	0.003	5.817
0.009998	0.004570	0.456	202.9	5.729	0.077	0.005	5.811
0.01013	0.005064	0.500	207.4	5.806	0.000	0.006	5.812
0.01005	0.006089	0.6011	217.4	5.975	-0.178	0.011	5.808
0.01016	0.006609	0.650	222.6	6.063	-0.269	0.015	5.811
0.09950	0.007460	0.7495	234.0	6.257	-0.476	0.030	5.811

Mean 5.811 ± 0.003

The measurements are recorded in Table 1. The value of $K_{s,2}(\text{gr.})$ was taken from the previous paper to be $10^{-8.10}$. The mean value found $K_{s,1}(\text{gr.}) = 10^{-5.811 \pm 0.003}$ is in very good agreement with the previously found value $10^{-5.80}$. The constancy of $K_{s,1}(\text{gr.})$ shows that only mononuclear hydrolysis products

Table 2. Changes in time of pH and extinction coefficients of cis-trans equilibrium mixtures made from cis-diaquo nitrate, and of solutions of "diol" nitrate

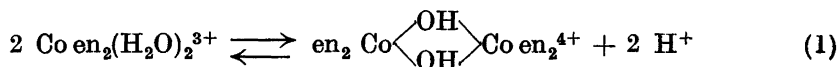
$$C_{\text{NaNO}_3} = 1.00 \text{ M}, 25^\circ \text{ C}$$

No	Salt	C_{Co}	$\bar{\nu}$	$-\log [\text{H}^+]$	Age in days	Vessel	540	520	500	440	420	410	380	360 m μ
1	diaquo	0.01074	0.252	5.336	1	paraff.	48.2	67.4	78.9	30.2	21.1	23.1	54.1	69.4
				5.283	95	"	48.8	67.6	80.6	30.6	20.7	22.6	54.7	71.0
				4.867	506	"	51.1	72.9	85.9	29.4	18.1	19.7	54.8	74.8
2	diaquo	0.01013	0.50	5.806	1	paraff.	50.9	66.6	74.5	31.0	26.6	30.9	59.8	69.7
				5.047	481	"	56.3	79.0	89.1	28.6	18.9	21.8	69.2	80.0
				6.673	1	Norite*	47.3	61.2	67.9	35.8	36.5	43.2	88.4	138.2
3	diol	0.00989	0.49	2.300	$t = 0$	glass	145.9	151.2	124.2	35.7	56.2	75.5	122.9	132.2
				5.839	13	"	52.4	68.3	75.6	31.2	27.4	32.0	61.4	71.4
				5.107	423	"	58.8	81.9	91.9	28.9	19.4	22.8	61.5	82.6
4	diaquo	0.00995	0.75	6.257	1	paraff.	54.7	67.8	71.4	31.9	31.9	38.5	66.1	71.7
				6.187	482	"	57.5	71.3	75.5	32.8	32.8	39.8	71.0	81.2
5	diaquo	0.00855	1.00	6.902	1	glass	58.9	70.1	70.5	33.4	37.2	45.9	73.6	76.5
				5.577	422	"	71.5	96.2	100.7	28.8	23.8	30.1	78.5	109.2
6	diol	0.00974	1.00		$t = 0$	glass	same spectrum as solution 3 at zero time							
				6.991	12	"	60.6	71.0	70.2	32.6	37.0	46.1	74.6	76.9
				5.747	422	"	70.2	93.7	97.8	28.1	24.0	30.4	76.0	99.8

* 50 ml of solution 2 were shaken with 0.035 g Norite charcoal for 20 hours in a thermostat at 25° C. The spectrum was taken after filtration from the charcoal.

are formed instantaneously. In the course of some weeks or months, however, the solutions show measurable changes. The rate of change is dependent upon the surface of the reaction vessel. Solutions stored in paraffined bottles change rather slowly and irregularly, one of them did not change at all in the course of 400 days. Solutions which were kept in ordinary glass bottles changed more rapidly. Charcoal has a striking effect. Evidently it catalyzes a splitting off of ethylenediamine as its effect is to decrease $[H^+]$. In Table 2 a selection of the experimental data is presented. It is seen from experiment No. 2 that both the spectral changes and the changes in $[H^+]$ in the solution treated with charcoal are quite different from those of the other experiments.

An explanation of the observed phenomena was first sought in the process:



and for testing this hypothesis the well-known tetrakis(ethylenediamine)- μ -dihydroxodicobalt(III) nitrate, Werner's "Diolsalt" was prepared. For shortness it is referred to as "diol" in the following.

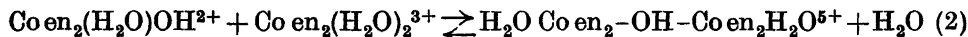
For solutions of this compound $\bar{\nu}$ is defined as the number of hydroxyl ions bound per cobalt atom after monomerization:

$$\bar{\nu} = \frac{C_{\text{Co}} - C_{\text{HNO}_3} + C_{\text{NaOH}} + [H^+] - [OH^-]}{C_{\text{Co}}}$$

if $|C_{\text{HNO}_3} - C_{\text{NaOH}}| \lesssim C_{\text{Co}}$.

Tables 2, 3 and 5 show that in solution the "diol" compound is decomposed to the monomeric system for all values of $\bar{\nu}$. Solutions of "diol" salt obtain in the course of some days an absorption spectrum which is identical with that of freshly prepared solutions of diaquosalt at the same $[H^+]$. Later on, the "diol" solutions in the buffer range change in the same way as do the solutions which are made up from the diaquosalt. These experiments definitely rule out the possibility of explaining the ageing process by equation (1).

Another simple explanation might be found in the reaction:



According to this mechanism the change in absorption spectrum should be greatest in solutions of $\bar{\nu} = 0.5$ and the hydrogen ion concentration should stay constant at this $\bar{\nu}$. Furthermore, it should decrease when $\bar{\nu} < 0.5$ and increase when $\bar{\nu} > 0.5$. It can be seen from Table 2 that this possibility must be ruled out too*.

As the results were not very reproducible and as a final equilibrium state was apparently never reached it seems meaningless to apply any of the elaborate theories of continuous polymerization *e. g.* those of Sillén². The *trans* ions have possibilities of forming chains while the *cis* ions might form large, strain-free rings but it seems impossible to give any satisfactory solution of the problem.

* In Abstracts of Papers of the XIIIth International Congress of Pure and Applied Chemistry, Stockholm 1953, the reaction (2) was suggested by us prematurely on the basis of preliminary experiments.

From the data in Table 2, however, one would be inclined to believe that the equilibrium cannot be displaced very far towards the polymer side*. This is supported by the fact that the aged solutions when acidified, develop the spectrum of the monomeric diaquo ions within a few minutes.

It is seen from Tables 2, 3 and 4 that the absorption spectrum of the "diol" is different in alkaline and in acid solution. Preliminary measurements showed that it is too weak an acid to have its dissociation constant determined accurately by glass electrode measurements but $K_{s,1}$ is probably of the order of magnitude 10^{-10} .

KINETICS OF THE DECOMPOSITION OF THE "DIOL" COMPLEX

The absorption spectra of the "diol" complex in alkaline solution and those of the *cis*- and *trans*-dihydroxobis(ethylenediamine)cobalt(III) ions do not differ very much, but we have tried to analyse the spectra obtained during the decomposition, assuming that the "diol" and the *cis*- and *trans*-dihydroxo ions were the only absorbing species present in the reacting mixture. A representative run is shown in Table 3. Using the observed extinction coefficients at the given wavelengths the concentration of each of the three species can be determined as the extinction coefficients of the pure species are known¹, but the accuracy is rather low. The result of such a computation is given in Table 4, where the distribution of the cobalt among the three species is estimated applying the method of least squares. The results seem to indicate that the *cis*-ion is formed first, and then slowly isomerizes (see Ref.¹) until equilibrium is obtained. This would be expected from the supposed configuration for the "diol" compound. A detailed kinetic investigation was not possible.

As mentioned above, the equilibrium in acidic solution is strongly displaced in favour of the *cis*-diaquo ions, which have an absorption spectrum differing considerably from that of the "diol" compound in the region 520—

Table 3. Decomposition of "diol" in alkaline solution.

$C_{Co} = 0.00510 M$, $C_{NaOH} = 0.0132 M$, $C_{NaNO_3} = 1.00 M$, $25^\circ C$.

$\bar{\nu} = 2$	Time in min.	560	540	520	500	380	370	360 $m\mu$
ϵ_{diol}	$t=0$ (extrapol.)	86.8	103.0	101.3	90.9	141.8	142.8	129.9
	128	69.5	88.5	96.0	85.7	116.8	120.7	111.0
	194	64.3	83.0	91.0	82.1	108.2	112.0	103.0
	244	62.6	81.0	89.5	81.0	104.8	108.0	100.2
	339	61.7	79.4	87.1	78.8	99.0	102.1	94.4
	$\sim 10^4$ (7 days)	46.6	63.6	71.5	64.8	77.0	78.9	73.1
ϵ_{eq}		46.7	63.8	71.3	64.6	75.5	77.3	71.5
ϵ_{cis}		55.4	82.1	93.0	85.5	97.5	103.6	95.5
ϵ_{tr}		38.6	49.3	53.0	48.1	54.9	53.9	50.5

* Because of the low solubility of the *trans* aquo hydroxo nitrate it was impossible to increase the cobalt concentration significantly.

Table 4. Estimated distribution of the cobalt on the species: Diol (α_{diol}), *cis*-dihydroxo (α_{cis}), *trans*-dihydroxo (α_{tr}) at various times in the experiment given in Table 3.

t (min.)	α_{diol}	α_{cis}	α_{trans}
0	1	0	0
128	0.482	0.470	0.048
194	0.371	0.491	0.138
244	0.321	0.513	0.166
339	0.264	0.509	0.227
$> 10^4$	0	0.444	0.556

560 $m\mu$, and there is an isobiestic point at 443 $m\mu$. The extinction coefficient of "diol" $\epsilon = 33.8$ at this wavelength is unchanged during the decomposition. Assuming that the "diol" and the *cis*-diaquo ion are the only species present in the reacting mixture, a degree of reaction $\alpha = \frac{\epsilon_{\text{diol}} - \epsilon}{\epsilon_{\text{diol}} - \epsilon_{\text{cis}}}$ can be calculated from the spectra (see Table 5). At a given time the degrees of reaction calculated from different wavelengths agree satisfactorily. Thus intermediate products can only exist in very small quantities.

The experiments were carried out in glass vessels before the different rates of polymerization in glass and in paraffin were found. Later on a single experiment showed that this reaction is also catalyzed by charcoal. It did not, however, seem worthwhile to repeat the measurements in paraffined bottles, as the experiments were fairly reproducible in glass apparatus. 1 *M* sodium nitrate was used as a constant salt medium in all cases.

The rate of decomposition in acidic solution is described by the following expression:

$$-\frac{dx}{dt} = k'(C_{\text{Co}}^0 - x)(C_{\text{H}^+}^0 + k'' - x)$$

Table 5. Decomposition of "diol" in acidic solution.

$C_{\text{Co}}^0 = 0.001792$ *M*, $C_{\text{HNO}_3}^0 = 0.004065$ *M*, $C_{\text{NaNO}_3} = 1.00$, 25° C.

$\bar{\nu} = 0$	Time in min.	560	540	520 $m\mu$	Average
ϵ_{diol}	$t = 0$ (extrapol.)	114.5	145.9	151.2	
	59.5	90.1	117.2	126.7	
$\alpha_{59.5}$		0.274	0.278	0.280	0.278
	98.0	75.5	99.9	112.7	
$\alpha_{98.0}$		0.437	0.445	0.440	0.441
	127.8	67.3	90.1	104.4	
$\alpha_{127.8}$		0.528	0.539	0.535	0.534
	169.8	57.8	79.6	95.2	
$\alpha_{169.8}$		0.635	0.641	0.640	0.639
	$\sim 10^4$ (7 days)	25.9	43.3	64.9	
ϵ_{cis}		25.5	42.8	64.6	

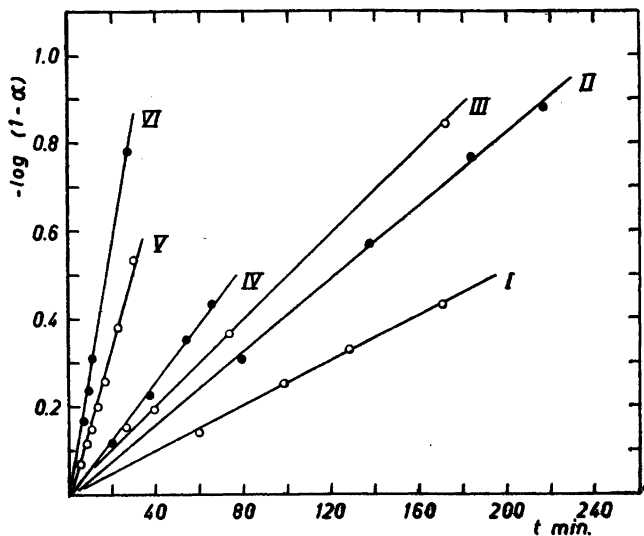


Fig. 1. $-\log(1-a)$ vs t in minutes. The slopes of the lines give preliminary values of $k_0 = k'k'' + k'(C_{\text{H}^+}^0 - C_{\text{Co}}^0)$. The compositions of the solutions ($C_{\text{H}^+}^0, C_{\text{Co}}^0$) are the following: I 0.00407 M, 0.00179 M, II 0.00813 M, 0.00188 M, III 0.0122 M, 0.00200 M, IV 0.0162 M, 0.00197 M, V 0.0500 M, 0.00203 M, VI 0.1004 M, 0.00150 M. $C_{\text{NaNO}_3} = 1.00 \text{ M}$ in all cases.

where $C_{\text{H}^+}^0$ is the initial concentration of hydrogen ions, C_{Co}^0 , moles of cobalt per liter, is the initial concentration of "diol" salt and x the concentration of cobalt transformed.

The integrated equation is

$$-\log(1-a) + \log \frac{C_{\text{H}^+}^0 + k'' - x}{C_{\text{H}^+}^0 + k''} = k' (C_{\text{H}^+}^0 - C_{\text{Co}}^0 + k'') t$$

where $a = \frac{x}{C_{\text{Co}}^0}$ is the degree of reaction calculated for "diol" in the experiment given in Table 5. The constants k' and k'' are obtained in the following way: First for each run $-\log(1-a)$ is plotted against t and preliminary values of $k_0 = k'k'' + k'(C_{\text{H}^+}^0 - C_{\text{Co}}^0)$ are obtained. This plot is given in Fig. 1. The k_0 's are plotted against $C_{\text{H}^+}^0 - C_{\text{Co}}^0$ and approximate values of k' and k'' are found. The k'' values are now inserted in the $\log \frac{C_{\text{H}^+}^0 + k'' - x}{C_{\text{H}^+}^0 + k''}$ term, and the left hand side of the integrated equation is plotted against t and new values of k_0 are found, which again give better values of k' and k'' . Already the second iteration gave no change in the constants and the following values were found using decadic logarithms: $k' = 0.030 \pm 0.002$ liter min.^{-1} equiv. $^{-1}$. $k'' = 0.0060 \pm 0.0015$ equiv. liter $^{-1}$.

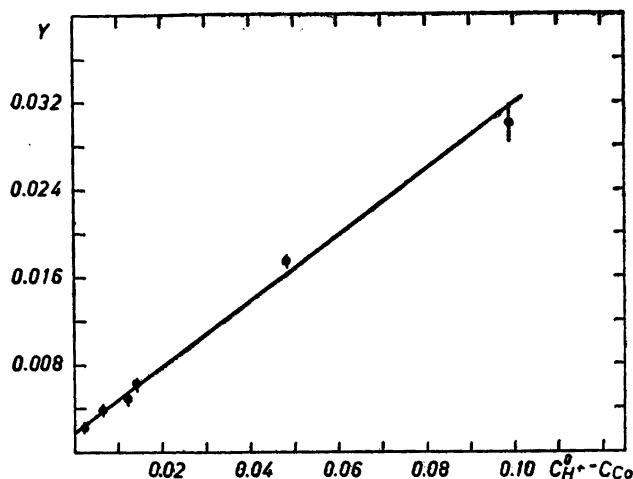
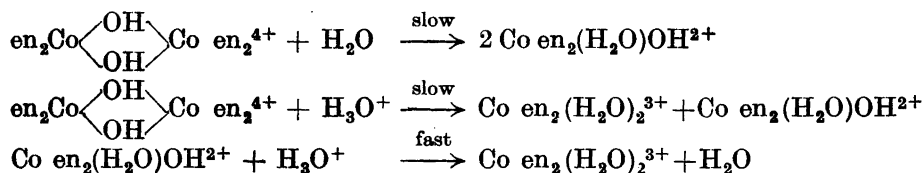


Fig. 2. $Y = -\frac{1}{t} \log(1-a) + \frac{1}{t} \log \frac{C_{H^+}^0 + k'' - x}{C_{H^+}^0 + k''}$ where $k'' = 0.0060$ equivalent. liter⁻¹ vs $C_{H^+}^0 - C_{Co}^0$. The slope of the line gives the value of k' and the intercept on the y-axis gives $k'k''$.

In Fig. 2 the experimental data are plotted using these two constants.

The rate expression found can be very simply interpreted as a combination of a "spontaneous" decomposition of the "diol" combined with a reaction with hydrogen ions:



It might, however, be more reasonable to assume that an intermediate containing only one hydroxyl bridge might be present in small concentrations: e. g. the ion $[\text{en}_2\text{Co}(\text{H}_2\text{O})-\text{OH}-(\text{H}_2\text{O})\text{Co en}_2]^{5+}$. Assuming that a steady state is rapidly obtained with constant concentration of this ion, the above mentioned rate equation is again obtained.

If this interpretation be true the rate of the "spontaneous" reaction in glass vessels at 25° and in 1 M NaNO₃ is given by $k'k'' = 0.00018$ min.⁻¹ and that of the reaction with hydrogen ions by $k' = 0.030$ liter min.⁻¹ equivalent.⁻¹.

EXPERIMENTAL

The *cis*-diaquobis(ethylenediamine)cobalt(III) nitrate was prepared and analysed as in Ref.¹ (Found: Co 13.92; N 23.11. Calc. for $\text{Co en}_2(\text{H}_2\text{O})_2(\text{NO}_3)_3, \text{H}_2\text{O}$: Co 14.06, N 23.39.)

The tetrakis(ethylenediamine)- μ -dihydroxodicobalt(III) nitrate was prepared according to Werner³ from *cis*-aquo-hydroxobis(ethylenediamine)cobalt(III) dithionate which was heated in an electric furnace at 110° C until constant weight was obtained.

The "diol" dithionate was obtained in this way but simultaneously another compound was formed which was insoluble both in acids and in bases. It is probably a high polymer although crystalline as shown by an X-ray diffraction pattern.

The "diol" nitrate was obtained from the dithionate *via* the bromide as described by Werner³. Contrary to Werner it was found to contain water. (Found: Co 18.12, C 14.52,

H 5.48, N 25.71. Calc. for $[\text{en}_2\text{Co} \begin{array}{c} \text{OH} \\ \diagdown \quad \diagup \\ \text{Co en}_2 \end{array} (\text{NO}_3)_4, 1/2 \text{H}_2\text{O}$: Co 18.16, C 14.80, H 5.43, N 25.89*.)

The glass electrodes were of the MacInnes and Dole type⁴. They were calibrated and found to have the theoretical response at 25° C. The hydrogen ion concentration was determined in all cases by standardizing against a standard acid solution of the composition $C_{\text{HNO}_3} = 0.005050$, $C_{\text{NaNO}_3} = 1.000$. The measurements were performed in a paraffin oil thermostat which controlled the temperature within $\pm 0.02^\circ \text{C}$. The valve potentiometer was a "Radiometer" Model PHM 3. The liquid junctions were established with cylindrical symmetry as recommended by Guggenheim⁵ using saturated KCl as a bridge solution. The whole set up was essentially similar to that used by Pedersen⁶.

In the kinetic experiments the reaction mixtures were kept in a water thermostat with a temperature control of $\pm 0.01^\circ \text{C}$.

The absorption spectra were measured on a Beckman DU spectrophotometer, the wavelength scale of which had been calibrated by aid of a mercury lamp. The cell compartment and the phototube were thermostated by aid of thermospacers. The molar extinction coefficient

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

(C_{Co} is the molar concentration of cobalt and d the thickness of the absorbing layer in cm) is given in all cases.

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