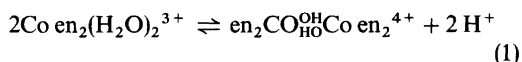# Studies on Polynuclear Complexes. II. On the Formation of Polynuclear Cobalt(III) Complexes in Aged Solutions of Aquahydroxo[tris(2-aminoethyl)amine]cobalt(III) Perchlorate

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Ageing reactions in solutions of aquahydroxo[tris-(2-aminoethyl)amine]cobalt(III) perchlorate have been studied. In our initial experiments we employed a temperature of 80 °C. However, the cobalt − nitrogen bonds were not sufficiently robust at this temperature and a series of unidentified decomposition products were formed during the ageing procedures. Experiments were therefore made at room temperature, the most important observation then being the slow formation of an orange-red polymer in 0.01 M solutions of the cobalt(III) monomers. A stationary state entailing transformation of up to 60 % of the cobalt into the polymer is established after about one year, and analysis of the aged solutions showed that no polymers other than the orange-red complex are formed in the diaqua-aquahydroxo buffer range. The isolated polymer is labile and is rapidly converted back into the monomers in acid solution. It has no acid-base properties in the pH range 4−9 and its absorption maxima (λ(nm), ε (l mol^{-1}cm^{-1}): 500,134; 355,113) are situated ~ 5 nm lower than those of the diaqua-(tren) complex. The polymer was not isolated in the solid state, but it could be estimated from the experiments that ~ 1.6 protons per cobalt monomer are set free when the polymer is formed from the diaqua tren complex and a plausible constitution consistent with this observation is discussed. Some Co−N bound-rupture occurs in the more basic solutions, tris{[di-μ-hydroxo(tren)]cobalt(III)}-cobalt(III) perchlorate being isolated as one of the products formed.

During a study [1,2] of the acid-base equilibria in the diaquabis(ethylenediamine)cobalt(III) system it was found that solutions of monomers in the buffer region showed spectral changes attended by a fall in pH in the course of a few weeks or months. It was first believed that this was due to the process:

$$2\text{Co en}_2(\text{H}_2\text{O})_2{}^{3+} \rightleftharpoons \text{en}_2\text{CO}^{\text{OH}}_{\text{HO}}\text{Co en}_2{}^{4+} + 2\,\text{H}^+ \tag{1}$$

However, the absorption spectrum of solutions prepared from tetrakis(ethylenediamine)di-μ-hydroxodicobalt(III) nitrate changed in the course of a few days until they became identical with that of solutions of the monomeric system at the pH in question. This clearly rules out the possibility of explaining the ageing process by eqn. (1).

The formation of chain or ring polymers of the type:

$$-\text{Co en}_2-\text{OH}-\text{Co en}_2-\text{OH}-\text{Co en}_2-\text{OH}-\text{Co en}_2-\text{OH}-$$
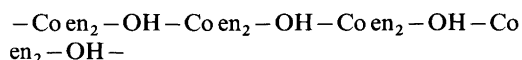
was another possibility. However, just as in "diol" formation, this type of polymerization cannot explain the fact that solutions of the aquahydroxobis(ethylenediamine) salt with one OH per cobalt monomer produce hydrogen ions during the polymerization process.

The two chelated ethylenediamine molecules were at first thought not to be engaged in the ageing reactions. However, it was noted that the

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solutions changed more rapidly in glass than in paraffined vessels and that addition of charcoal had a striking effect. Charcoal evidently catalyzes dissociation of ethylenediamine with the results that the solutions instead of becoming more acidic became more basic. The experiments mentioned were all performed at room temperature, but some subsequent experiments performed by Sven Harnung of this department have shown that the use of higher temperatures also results in some decomposition of the complexes leading to an increase in pH.

In the hope of avoiding such decomposition we have studied the ageing reactions occurring in the analogous cobalt(III) system with the tetradentate ligand tris(2-aminoethyl)amine (in the following abbreviated tren). This ligand has the advantage for our purposes that it occupies four facial positions for steric reasons, so that only two *cis* positions are left for the ageing reactions, assuming that the Co − N bonds are sufficiently robust.

In order to obtain results in a reasonably short time, our first experiments with the cobalt(III) tren complexes were made at 80 °C. However, contrary to expectations some cobalt-nitrogen bond rupture took place at this temperature and separation of the reaction mixture on Sephadex columns showed that a complex mixture of unidentified products was formed. In the following section the experiments at
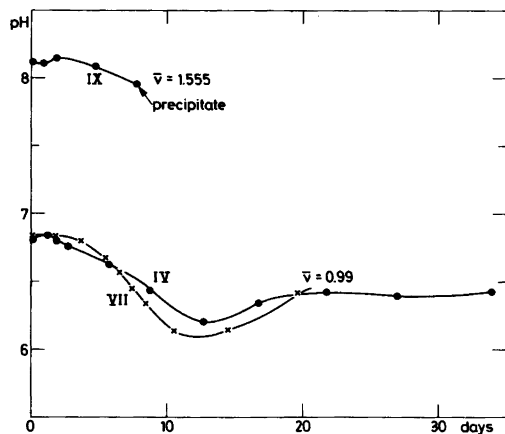
80 °C are dealt with. We then describe the more successful experiments at room temperature, in which cobalt-nitrogen bond rupture was unimportant in relation to the ageing reactions.

Ageing experiments with the cobalt(III)tren complexes in 1 M NaClO₄ at 80 °C. The solutions of the aqua-hydroxo complex were made up in 1 M NaClO₄ from the anhydrous perchlorate salt, [Co tren(OH)H₂O](ClO₄)₂. Solutions of this salt with or without addition of HClO₄ and (or) NaOH are characterized in the following by their cobalt concentration C_{Co} and by $\bar{v}$, the average number of protons released initially per cobalt atom:

$$\bar{v} = \frac{C_{Co} - C_{HNO_3} + C_{NaOH} + [H^+] - [OH^-]}{C_{Co}} \quad (2)$$

if $|C_{HNO_3} - C_{NaOH}| \lesssim C_{Co}$.

The way in which the ageing reactions influence pH in ~0.01 M complex solutions with different $\bar{v}$ is shown in Fig. 1. The reactions are surface catalyzed and therefore not completely reproducible. However, Fig. 1 shows clearly that the initial
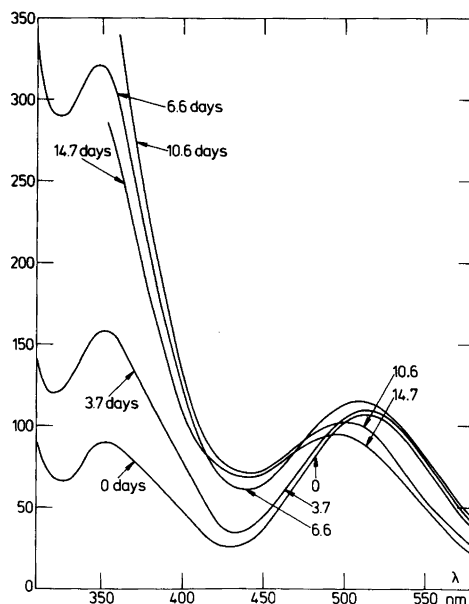
Fig. 2. Changes in the absorption spectrum of solution VII ($C_{Co} = 0.0128$ and $\bar{v} = 0.99$) during the ageing process at 80 °C. Samples were taken at intervals and measurements made at 25 °C. The figures on the curves indicate the number of days from the start of the experiment.

Fig. 1. The change in pH with time at 80 °C for solutions with various $\bar{v}$. $C_{NaClO_4} = 1.00$ M in the solutions and the cobalt concentrations C_{Co} were as follows: IV, 0.00997; VII, 0.01028; IX, 0.00965 M. The measurements were made at 25 °C on samples taken at intervals.

reactions for solutions with $\bar{v} = 0.99$ and 1.555 produce a decrease in pH which is followed after some days by reactions which increase pH, and which for $\bar{v} = 1.555$ lead to precipitation.

The effect of the ageing reactions on the absorption spectrum of solution VII with $\bar{v} = 0.99$ is shown in Fig. 2. The band in the visible region shows, like the changes in pH, two opposite effects: first a small intensity increase followed, after about one week, by a decrease, the absorption maximum in both cases shifting towards lower wavelength. On the other hand, the very large increase in the ultraviolet absorption intensity suggests extensive decomposition of the complexes.

In the case of solution VII the formation of a very complex mixture of compounds during the ageing reactions was shown directly by separation on Sephadex columns. Some analytical results from this experiment, in which the percentage of cobalt in each fraction was determined by atomic absorption spectrometry (see Experimental), are shown in Table 1. It can be seen that at least six coloured fractions are formed in the solution after keeping it at 80 °C for about 12 days.

Table 1. Separation of the components of solution VII ($\bar{v} = 0.99$) at various stages of the ageing process. 0.2 – 0.6 M $NaClO_4$ solutions (pH ~ 3) were used as eluent.

Days	Colour of fractions	Co %
3.7	red	93
	orange-red	weak
	violet	~ 1
6.6	orange-red	13
	red	86
	reddish brown	2
	greyish	Residue
7.5	orange-red	31
	red	67
	brown	4
	greyish	Residue
12.5	violet	38
	orange-red	20
	reddish brown	2
	violet	20
	yellow	8
	brown	11
	greyish	Residue

Their presence is indicative of the existence of a number of new polymeric cobalt(III) complexes, although identification of these will require further work. However, the red fraction dominating during the first week of the reaction can be ascribed to the equilibrium mixture of the monomeric cobalt(III) tren complexes. It should be noted that an orange-red fraction appears to be the initial reaction product. This compound will be dealt with in more detail in the following section.

Results of the ageing experiments at room temperature. Portions of solutions Nos. I – X which were to be used in the experiments at 80 °C were set aside and used to follow the slow ageing reactions at room temperature. Changes in pH and extinction coefficients for solutions Nos. I – VII (having $\bar{v} \sim 0.5$ and ~ 1.0) after about 500 days are described in Table 2. All of these solutions have become considerably more acidic during the 16 months in which they have been maintained at room temperature. It is also noteworthy that the five solutions having $\bar{v} \sim 1$ and C_{Co} varying from 0.005 to 0.02 M have exhibited very similar pH- and extinction coefficient changes. It is known from the separation experiments on Sephadex columns that apart from the mononuclear complexes only one polymer is formed in the solutions having $\bar{v} \lesssim 1$. This polymer is probably identical with the orange-red complex formed initially in the experiments at 80 °C, and it should be mentioned that after 500 days solution I was found to contain $\sim 21 \%$ of the cobalt in the form of this polymer, $\sim 75 \%$ in the mononuclear aquahydroxo system, and only about 3% as unidentified residue. By making certain assumptions it should therefore be possible to calculate the spectrum of the polymer from the data given in Table 2.

Calculation of the absorption spectrum of the orange-red polymer. In order to calculate the spectrum of the orange-red polymer it is necessary to know the number of protons per cobalt which are released during its formation. For this purpose we know that solutions VIII and IX in Table 5, both having $\bar{v} \sim 1.5$, become more acidic during the ageing process, whereas solution X having $\bar{v} = 1.9$ becomes more basic. We have therefore tentatively assumed that 1.6 protons per cobalt are released during the formation of the polymer from the diaqua tren complex.

If we denote the formal cobalt concentration in the polymer by x and the average number of protons released from the diaqua complex in the

Table 2. Extinction coefficients for the diaqua-, dihydroxo- and aquahydroxotren cobalt(III) ions, and the changes in pH and extinction coefficients during ageing of solutions I–VII with $\bar{v} \leqq 1.00$. $C_{NaClO_4} = 1.00$ M, 25 °C.

Solution	C_{Co}	$\bar{v}$	pH	days	560	530	510	490	450	430	410 nm
Diaqua	0.00809	0	~2	0	47.0	90.0	107.1	101.6	41.8	19.8	17.9
Dihydroxo	0.00798	2	~11	0	77.0	116.0	117.0	92.8	28.7	21.6	44.9
Aquahydroxo	–	1	–	0	69.0	103.4	110.0	95.0	38,2	27.7	40.1
I	0.01006	0.494	5.68	0	55.5	95.0	110.0	100.8	41.7	25.2	28.6
	0.01006	0.494	5.68	21	55.8	95.0	109.4	99.4	40.7	24.4	28.8
	0.01006	0.494	4.86	499	48.2	95.5	115.1	108.2	43.7	22.4	23.8
II	0.00994	0.591	5.83	0	58.5	97.5	110.0	100.1	36.0	30.6	30.6
	0.00994	0.591	4.93	499	49.3	98.8	118.5	111.9	44.3	22.2	24.6
III	0.00515	0.979	6.79	0	68.0	104.3	112.5	97.3	38.9	29.5	39.0
	0.00515	0.979	5.12	500	48.5	104.9	130.0	123.1	48.5	25.2	29.1
IV	0.00997	0.989	6.82	0	68.4	103.4	111.4	95.4	37.4	26.9	39.1
	0.00997	0.989	5.12	500	49.1	103.1	125.2	116.2	44.1	24.1	30.1
V	0.01992	0.997	6.85	0	67.3	103.4	112.4	95.2	36.9	26.9	38.7
	0.01992	0.997	5.12	500	52.1	(106)	–	–	48.2	26.2	32.6
VI	0.01007	0.969	6.75	0	68.0	104.0	113.0	98.3	39.1	28.3	37.2
	0.01007	0.969	5.19	499	51.7	106.2	131.0	122.0	46.9	26.0	31.5
VII	0.01028	0.991	6.83	0	62.2	98.8	106.1	–	36.4	25.6	37.0
	0.01028	0.991	6.70	20	68.5	104.8	113.0	97.8	40.4	30.3	43.5
	0.01028	0.991	519	470	49.8	104.4	129.2	122.5	48.5	27.2	32.6

equilibrium system of the monomers by $\bar{n}$, we obtain the following equation which is valid subject to the assumptions made:

$$\bar{v} C_{Co} = \bar{n}(C_o - x) + 1.6x$$

or

$$x = \frac{C_{Co}(\bar{v} - \bar{n})}{(1.6 - \bar{n})} \qquad (3)$$

From this expression x can be calculated. C_{Co} and $\bar{v}$ are known for the initial solutions, and $\bar{n} = \alpha_1 + 2\alpha_2$ as well as the fractions of diaqua (α_0), aquahydroxo (α_1) and dihydroxo (α_2) ions can be calculated from the pH in the aged solutions and the dissociation constants of the diaqua ion: $pK_1 = 5.69$, $pK_2 = 8.04$ (see Experimental).

If we furthermore introduce the molar extinction coefficients of the diaqua (ε_0), aquahydroxo (ε_1) and dihydroxo (ε_2) ions at a given wavelength, the extinction coefficient (ε_x) of the polymer at this wavelength can be calculated from eqn. (4).

$$x\varepsilon_x = C_{Co}\varepsilon_{av} - (C_{Co} - x)(\alpha_0\varepsilon_0 + \alpha_1\varepsilon_1 + \alpha_2\varepsilon_2) \qquad (4)$$

where ε_{av} is the experimental extinction coefficient for the aged solutions. The values of ε_0 and ε_2 given in Table 2 were measured directly for acidic and basic solutions, and the value of ε_1 was calculated from the average spectrum of the solutions having $\bar{v} \sim 0.99$ and the following distribution of the complexes: $\alpha_0 = 0.064$, $\alpha_1 = 0.882$, $\alpha_2 = 0.054$.

Results of the calculations for solutions I–VII are shown in Table 3. The fraction $\alpha_x = x/C_{Co}$ of the polymer varies from 0.25 for $\bar{v} \sim 0.5$ to as much as ~ 0.6 for $\bar{v} = 1$. The value $\alpha_x = 0.25$ for solution I is seen to be in good agreement with the value of 0.21 obtained in the previously-mentioned direct determination employing Sephadex columns. It should also be noted that there is fair agreement between the values of the extinction coefficients for the polymer calculated for the various solutions.

Table 3. Calculated extinction coefficients for the orange-red polymer in aged solutions of the cobalt(III) tren system.

No.	C_{Co}	$\bar{v}$	$\bar{n}$	x	560	530	510	490	450	430	410 nm
I	0.01006	0.494	0.129	0.00250	43	106	138	132	51	27	34
II	0.00994	0.591	0.147	0.00303	47	113	145	136	51	24.7	33
III	0.00515	0.979	0.214	0.00292	46	114	147	141	54.5	28.1	34
IV	0.00997	0.989	0.213	0.00565	46	109	136	127	46	25.6	35
V	0.01992	0.997	0.212	0.01130	52	122	142	140	53.5	29.2	41
VI	0.01007	0.969	0.242	0.00563	69	117	149	140	51.5	28.4	45
VII	0.01028	0.991	0.239	0.00575	46	113	146	140	55	31.5	40

Table 4. Calculated extinction coefficients for the hypothetical polymer in aged solutions of the cobalt(III) bis(ethylenediamine) system (based on data given by Rasmussen and Bjerrum [2]). Extinction coefficients of the *cis-trans* equilibrium mixture of the monomers are also given.

C_{Co}	$\bar{v}$	pH	$\bar{n}$	x	540	520	500	440	420	410	380 nm
0.01013	0.50	5.047	0.147	0.00246	93	126	124	24	21	31	134
0.00989	0.49	5.837	0.166	0.00223	106.5	143	140	24.6	22	34	104
0.00855	1.00	5.577	0.371	0.00438	93	125	124	26.7	24.4	26.2	101
0.00974	1.00	5.747	0.468	0.00457	92	124	123	24.7	22.5	32	96.6
				Average	96	129	128	25	22.4	30.8	109
				Diaqua	41.6	62.6	79.4	29.6	14.9	14.2	44.0
				Dihydroxo	63.6	71.0	65.6	20.6	24.2	37.0	73.6
				Aquahydroxo	61.5	71.2	71.1	32.9	37.4	46.2	73.6

An analogous calculation of the extinction coefficients of a corresponding hypothetical polymer in aged solutions of the cobalt(III) bis(ethylenediamine) system was made using the data given by Rasmussen and Bjerrum.[2] The results of such a calculation for solutions showing a sufficient change in pH during ageing for more than 400 days (solutions 2, 3, 5 and 6) are shown in Table 4. The values for the extinction coefficients of the equilibrated *cis/trans* diaqua, dihydroxo and aquahydroxo monomers used in the calculation are also also given. Eqns. (3) and (4) were used, and the calculations of α_0, α_1, α_2 and $\bar{n}$ were made using the following dissociation constants for the *cis/trans* equilibrated diaqua ions: $pK_1 = 5.81$, $pK_2 = 8.10$ (1 M KNO₃, 25 °C).[1]

The absorption spectrum and extinction coefficients estimated for the orange-red polymeric tren and ethylenediamine species are compared in Fig. 3 with the spectra of the corresponding diaqua and dihydroxo monomers.

Direct measurements of the spectrum of the orange-red tren cobalt(III) polymer. Data for the solutions

used for these measurements are given in Table 5. The aged solutions are probably all very close to being at equilibrium. For example, it was observed that the spectrum of VIII did not change significantly after about 400 days. During the first year of ageing solutions VIII and IX, both having $\bar{v} \sim 1.5$, deposited a few milligrams of irregular, almost black crystals. These crystals were identified by analysis and by their solution spectrum (λ_{max} 622, 495 and 310 nm) as tris{[di-μ-hydroxo(tren)]cobalt(III)}-cobalt(III) perchlorate, analogous to the so-called "Werner's brown salts",[3] (see Experimental).

The aged solutions referred to in Table 5 were analyzed on Sephadex columns and the results are summarized in Table 6. The first fractions contained the orange-red polymer and the second fractions the equilibrium mixture of the monomers. It will also be noted that the orange-red polymer is so labile that a change in the pH of the eluent from ~ 5 to ~ 2 (in the case of solution IX) reduces the percentage of isolated polymer from 66 to 10 % and increases the percentage of the aquahydroxo mixture from 6 to 72 %. The violet labile third frac-
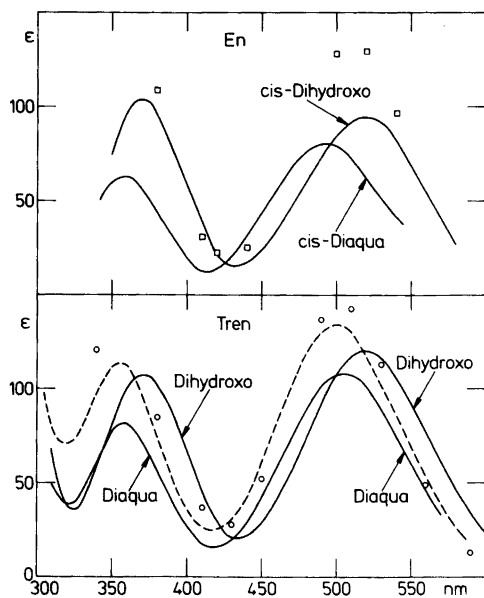
Fig. 3. The lower part of the figure shows the directly-measured spectrum of the orange-red polymer (– – –) and of the diaqua- and dihydroxo(tren)-cobalt(III) complexes. The ○-points show the extinction coefficients (from Table 3) for the polymer calculated on the basis of data for the aged solutions.

The upper part of the figure shows the spectra of the *cis*-diaqua- and *cis*-dihydroxobis(ethylenediamine)cobalt(III) complexes, and the □-points show the calculated values (from Table 4) for the hypothetical polymer formed in aged bis(ethylenediamine)cobalt(III) solutions.

Table 5. Data for solutions of the aquahydroxo-(tren)cobalt(III) salt in 1 M NaClO$_4$ ($\bar{v} > 1$) aged at room temperature.

No.	C_{Co}	$\bar{v}$	pH	Time of ageing (days)
VIII	0.00942	1.437	7.43	0
	0.00866	–	6.42	866
IX	0.00965	1.555	8.14	0
	0.00936	–	6.70	816
X	0.00788	1.90	9.02	0
	0.00788	–	9.53	383

Table 6. Sephadex column separations of the components of the aged solutions referred to in Table 5. 0.15 – 0.7 M NaClO$_4$ solutions were used as eluents for VIII and IX, and 0.2 – 0.5 M NH$_4$Cl,NH$_3$ buffer solutions for X. Figures give the percentage of total cobalt present.

pH in eluent	VIII ~5	IX ~5	IX ~2	X ~9
1. Fraction, % Co	52	66	10	62
2. Fraction, % Co	44	6	72	11
3. Fraction, % Co	–	16	4	4
Left on column, % Co	5	12	14	23

tion obtained from solution IX could not be identified. The brownish-yellow third fraction obtained from solution X was found to contain tris{[di-μ-hydroxo(tren)]cobalt(III)}cobalt(III) complex. The amount of higher polymers and decomposition products left on the columns, which was negligible in the case of the more acidic solutions for $\bar{v} \lesssim 1$, is seen to increase with increasing basicity of the solutions.

The absorbance and the cobalt concentration of isolated fractions of the orange-red polymer were measured in several cases, and the extinction coefficients obtained are summarized in Table 7. It is especially noteworthy how well the extinction coefficients estimated indirectly from measurements on solutions I – VII (Table 3) agree with the directly measured extinction coefficients obtained for the isolated polymer fractions from solutions VIII – X. The best spectrum, especially in the ultraviolet part of the spectrum, was observed for a polymer fraction from solution X in which the cobalt concentration had been increased about 10 fold by repeated elution.[4] The lack of acid-base properties, and the essential constancy of the absorption spectrum (within ≤ 1 %) of the orange-red polymer in the pH-range 4 to 9 was also established using this fraction. Unfortunately the cobalt concentration in this fraction was poorly determined and the extinction coefficients have therefore been fitted to the other data by assuming $\varepsilon_{510} = 130$ l mol^{-1} cm^{-1}.

The orange-red polymer is very labile at low pH as can be seen from the data shown in Table 6 and decomposes in acidic solution to give the diaqua-(tren) complex.

The solutions employed in the experiments discussed until now all had C_{Co} ~0.01 M. More pronounced polymer formation would be expected

Table 7. Comparison of calculated and directly measured molar extinction coefficients for the orange-red cobalt(III) tren polymer. C_{Co} in the isolated fractions varied from 0.3 to 0.7 mM in VIII and IX, to ~5 mM in X.

No.	Method	560	530	510	490	450	430	410 nm
VIII	Direct	52	100	125	122	62.5	46	54
IX	Direct	44	103	134	128	52	30	38
X	Direct	54	104	(130)	130	61	32	27
I–VII	Calc.	49	113	143	137	52	28	37

in solutions with a higher cobalt concentration and to examine this a solution having $C_{Co} = 0.067$ M and $\bar{v} = 1.5$ was studied. The results of the analysis of this solution after ageing for 380 days are shown in Table 8. It can be seen that as many as 7 fractions are obtained in this case. The first fraction contains the orange-red polymer and the second fraction the equilibrium mixture of the monomers. Of the other fractions only the 7th, showing maxima at 620, 426 and 308 nm, could be identified as containing the tris{[di-μ-hydroxo(tren)]cobalt(III)}cobalt(III) complex. Considerably more work will be necessary to identify (and if possible obtain solid salts of) the complexes present in the remaining fractions. In this connection it can be mentioned that an attempt to isolate the iodide salt of the labile orange-red polymer led to the precipitation after some hours of a small quantity of crystalline material which was analyzed for aquahydroxo(tren)cobalt(III) iodide.

DISCUSSION

The main result of the work described here is the observation of the slow formation of an orange-red polymeric complex in dilute (~0.01 M) solutions of the aquahydroxo(tren)cobalt(III) system. A stationary state involving up to 60 % of the cobalt in the form of the polymer is attained after about one year at room temperature. Furthermore, analysis of aged solutions of the monomeric system having a neutralization degree $\bar{v} \le 1$ has shown that no polymers other than the orange-red species are formed at room temperature. Solutions with $\bar{v} \simeq 1.5$ become more acidic, and solutions with $\bar{v} = 1.9$ more basic during the ageing process (see Table 5). Some formation of other complexes occurs in aged solutions with $\bar{v} \ge 1.5$, but there is nothing to indicate that tren functions as a tridentate ligand by the formation of the orange-red polymer. The cobalt(III) ions must therefore have only two co-ordination sites remaining for bridged complex formation and this restriction reduces the number

Table 8. Analysis of a more concentrated cobalt(III) tren solution ($C_{Co} = 0.067$ M, $\bar{v} = 1.5$) aged at room temperature for about 380 days. NaCl solution was used as eluent.

No. of fraction	Co %	Colour of fraction	pH	Band maxima (λ in nm)			$\varepsilon(\sim 500)/\varepsilon(\sim 360)$
1	~35	orange-red	4–9	500,	354		~1.25
2	~5	as monomers	4	500,	358		~1.32
			9	508,	358		~1.25
3	~30	red	4	508,	361		~1.3
			9	513,	362		~0.85
4	~25	violet	4–9	523,	360		~1.25
5	~1.3	red	4–9	510,	~365		
6	~1.2	blue	4–9	528,	368		~1.0
7	~0.5	brownish	4–9	620,	496,	308	
Residue	~2	red					

Table 9. Absorption maxima for some cobalt(III) tren complexes.

Complex	$\lambda_{max,1}$	ε	$\lambda_{max,2}$	ε	$\lambda_{max,3}$	ε	Reference
Orange polymer	500	134	355	113			This paper
Co tren(H$_2$O)$_2$$^{3+}$	505	107.5	360	81			This paper
	504	109	360	81			Scheidegger [5]
Co tren(OH)H$_2$O^{2+}	512	110	355	82			This paper
	513	100	355	65			Bösch [6]
Co tren(OH)$_2$$^+$	520	120	370	107			This paper
	520	119	370	117			Scheidegger [5]
{tren Co(OH)$_2$Co tren}$_3$$^{4+}$	526	129	368	170 .	300	3890	Bösch [6]
Co{(OH)$_2$Co tren}$_3$$^{6+}$	622	117	495	372	310	6020	This paper
	623	135	500	468	311	7410	Bösch [6]

of possibilities for the constitution of the complex. The proposal expressed by eqn. (5) corresponding

$$Co\ tren(OH)H_2O^{2+} + 2Co\ tren(OH)_2^+ \rightarrow$$
$$O(Co\ tren\ OH)_3^{4+} + 2H_2O \qquad (5)$$
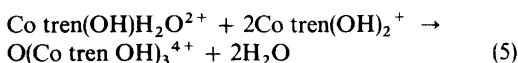
to $\bar{v} = 1.67$ is consistent with the data. In Fig. 3 (lower part) the absorption spectrum of the polymer is compared with those of the diaqua and dihydroxo-(tren)cobalt(III) complexes. The data for the absorption maxima are given in Table 9 and it will be noted that the absorption maxima for the polymer are situated ~ 5 nm lower than those for the diaqua tren complex. This is consistent with the orange colour of the polymer and supports our assumption that the four $Co - N$ bonds remain intact during the formation of the polymer. However, the relatively low absorption intensity in the ultraviolet may not support our assumption (*cf.* Table 9). Furthermore, although the ease with which the polymer is eluted from Sephadex columns is consistent with a relatively low charge per cobalt atom, we have still to explain the fact that the three OH-groups in the proposed polymer do not show acid-base properties in the pH-range $4 - 9$. As regards the latter problem, it is possible that the compound has a structure in which the three OH-groups are strongly hydrogen bonded to each other. To bring them within bonding distances the angle $Co - O - Co$ has to be $120 - 125°$, compared to $115°$ in H_3O^+. In the basic chromium-(III) acetate, $O\left(Cr\left\{{O \atop O}\right\}>CCH_3\right\}_2H_2O\right)_3^+$, the three chromium atoms and the central oxygen lie in the same plane,[7] but this is not a prerequisite in the case of diamagnetic cobalt(III) structures with no possibility of stabilization *via* π-bonding. A model of $O(Co\ tren\ OH)_3^{4+}$ with a distance from cobalt to

the central oxygen atom of 2.0 Å shows, however, that the structure is so compact that only with difficulty is it possible to place the coordinated NH_2-groups sufficiently far apart, *e.g.* 2.7 Å, from each other. On the other hand, the assumptions made are consistent with the fact that the polymer slowly undergoes changes when isolated from the solution in which it is formed and rapidly hydrolyzes to give the monomers in acidic solution.

The spectra of the diaqua- and dihydroxobis-(ethylenediamine)cobalt(III) complexes and the λ,ε-values calculated for the hypothetical polymer in this system from the data of Rasmussen and Bjerrum[2] (see Table 4) are shown in the upper part of Fig. 3. The data provide some support for the proposal that this polymer has a constitution similar to that of the orange-red polymer in the tren system, but this remains to be confirmed by direct isolation of the polymer.

EXPERIMENTAL

Preparation of complexes. Aquahydroxo(tren)-cobalt(III) perchlorate was prepared from the corresponding carbonato complex:

$[Co\ tren(CO_3)]ClO_4.aq$ has been prepared previously by Scheidegger.[5] Our procedure was as follows: A solution of CoCl$_2$.6H$_2$O (23.8 g, 0.1 mol) in a mixture of 30 % H$_2$O$_2$ (50 ml) and water (250 ml) was slowly added to solid KHCO$_3$ (100 g). The green mixture was heated and vigorously stirred. After 10 min solid tren.3HCl (25.4 g, 0.1 mol) was added in small portions. The solution became reddish-brown and after heating for 10 min all the solid had dissolved. The solution was then evaporated to about one half of its original volume and after cooling to room temperature three volumes of methanol were added. About 90 % of the KCl

was precipitated in this way and after filtration the methanol was removed from the solution by evaporation and the remaining chloride by adding 0.2 M AgClO$_4$ dropwise until precipitation ceased. The mixture was filtered and after adding 3.5 M LiClO$_4$ (100 ml) the solution was cooled in ice and the carbonato perchlorate precipitated by adding ethanol (500 ml). The dark red crystals of [Co tren(CO$_3$)]ClO$_4$.2H$_2$O were washed with ethanol and dried in air. The crude product was purified as follows: 50 g of the salt was stirred mechanically with 150 ml of 99 % ethanol for 1 h in order to remove the remaining LiClO$_4$. After filtration the procedure was repeated twice.

[Co tren(OH)H$_2$O](ClO$_4$)$_2$. [Co tren(CO$_3$)]-ClO$_4$.2H$_2$O (40 g, 0.1 mol) was dissolved in the minimum volume of water at 80 °C and 5 M HClO$_4$ was then added dropwise until CO$_2$ evolution ceased. The solution was maintained at 80 °C for a further 30 min and allowed to cool. After addition of saturated NaClO$_4$ (20 ml) the ice-cold solution was slowly neutralized by addition of 2 M NaOH. At pH 5–6 [Co tren(OH)H$_2$O](ClO$_4$)$_2$ began to precipitate as red-violet crystals. Continuing with the neutralization 95–98 % of the salt could be precipitated. The crystals were washed with ethanol and recrystallized from water. Anal. Calc. for Co tren(OH)H$_2$O(ClO$_4$)$_2$: Co 13.42; C 16.14; H 4.82; N 12.76; Cl 16.15. Found: Co 13.39; C 16.26; H 4.79; N 12.81; Cl 15.94.

Co{(OH)$_2$Co tren}$_3$(ClO$_4$)$_6$, which separated from some of the aged solutions of the cobalt(III) tren monomers, has recently been characterized by Bösch[6] (see Table 9). The following preparative route has been devised by us: Co(ClO$_4$)$_2$.6H$_2$O (18.0 g, 0.05 mol) was dissolved in water (25 ml) and tren (5.6 g, 0.0375 mol) was added and the dark red mixture was filtered to remove a slight precipitate of cobalt oxide. The solution was stirred vigorously and aerated for 2 h and was then placed in a refrigerator at 5 °C. After 5 days the precipitate of crude Co{(OH)$_2$Co tren}$_3$(ClO$_4$)$_6$.aq (9.8 g) was isolated by filtration. The salt was recrystallized from water at 60 °C.

The dark brown irregular crystals were subjected to an X-ray analysis by Mrs. Eva Bang. They crystallize in the monolinic system with the unit cell dimensions $a = 23.67$ Å, $b = 13.47$ Å, $c = 32.96$ Å and $\beta = 98.22°$. Weissenberg photographs show an ordered-disordered structure and oscillation diagrams around the b-axis clearly show equatorial symmetry.

Solutions. The solutions of cobalt(III) tren complexes in 1 M NaClO$_4$ were prepared by weighing the complex salt and pipetting or titrating from stock solutions of NaClO$_4$ (5 M), HClO$_4$ and NaOH.

pH-Measurements. Hydrogen ion concentrations were measured relative to $10^{-3} - 10^{-2}$ M solutions of HClO$_4$ in 1 M NaClO$_4$, using a Radiometer PHM 52 digital pH-meter. A selected Radiometer glass electrode (type 620 2 B) with the theoretical pH-dependence was used, and a 1 M NaCl/calomel electrode was employed as reference.

The acid dissociation constants of the diaqua(tren)-cobalt(III) complex were determined according to the method of Bjerrum and Rasmussen[1] from measurements of the hydrogen ion concentration in a number of solutions having $\bar{v} \sim 0.5$ and $\bar{v} \sim 1.5$. The following values were obtained: p$K_1 = 5.69$, p$K_2 = 8.04$ (1 M NaClO$_4$, 25 °C).

Spectrophotometric measurements. The absorption spectra were measured on a Cary 14 spectrophotometer with a thermostatted (25 °C) cell compartment. In a few cases a Cary 118 spectrophotometer was also used. Cells of pathlength 0.1 to 5 cm were used, the reference cells being filled with 1 M NaClO$_4$ solution.

Analysis. The Co(III) species in the aged solutions were separated by cation-exchange chromatography on columns of Sephadex SP C-25. When necessary the eluates were concentrated employing the technique used by Andersen et al.[4] The cobalt content in the various fractions was determined by atomic absorption spectrometry using a Perkin-Elmer, model 403, instrument.

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