

## Synthesis of $(-)_589$ -Di- $\mu$ -hydroxo- $\Delta$ -bis(ethylenediamine)-chromium(III)- $\Delta$ -bis(ethylenediamine)cobalt(III) Perchlorate

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Heating of the cocrystallized dithionates of the cations  $\Delta$ -*cis*-[Cr(en)<sub>2</sub>(OH)(H<sub>2</sub>O)]<sup>2+</sup> and  $\Delta$ -*cis*-[Co(en)<sub>2</sub>(OH)(H<sub>2</sub>O)]<sup>2+</sup> yielded nearly quantitatively  $(-)_589$ - $\Delta$ , $\Delta$ -[(en)<sub>2</sub>Cr(OH)<sub>2</sub>Co(en)<sub>2</sub>](S<sub>2</sub>O<sub>6</sub>)<sub>2</sub>, from which pure  $(-)_589$ - $\Delta$ , $\Delta$ -[(en)<sub>2</sub>Cr(OH)<sub>2</sub>Co(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was obtained by a kinetically controlled fractionation procedure.

Di-hydroxo bridged binuclear complexes (diols) with chromium(III) or cobalt(III) have been known for many years and the classical tetraammine and bis(ethylenediamine) diols<sup>1-4</sup> are still among the most studied ones. The structure of these have now been established by single crystal X-ray structural analysis of [(NH<sub>3</sub>)<sub>4</sub>Co(OH)<sub>2</sub>Co(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>·4H<sub>2</sub>O<sup>5,6</sup> and  $\Delta$ , $\Delta$ -[(en)<sub>2</sub>Cr(OH)<sub>2</sub>Cr(en)<sub>2</sub>]Cl<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O<sup>7</sup> and Guinier X-ray powder diffraction studies.<sup>8</sup> These complexes (and their parent mono-ols, *vide infra*) therefore represent bridged structures of known constitution, whose properties may throw light upon the most common type of hydrolysis products of aqua ions within the whole periodical system.

The kinetics and the thermodynamics of the hydrolysis of the chromium(III) and cobalt(III) diols to their parent mono-nuclear complexes have been studied several times but are still in many respects not understood.<sup>9-14</sup> The proposed reaction mechanisms all involve a mono-hydroxo bridged intermediate (*mono-ol*). The existence of such an intermediate has recently been unambiguously established<sup>15,16</sup> in the chromium(III) bis(ethylenediamine) system in which equilibration between mono-ols and diol is established within minutes at room tempera-

ture, *i.e.* long before the occurrence of other reactions confuse the issue. The mono-hydroxo bridged structure of the intermediate has very recently been further established by a single crystal X-ray structural analysis on  $\Delta$ , $\Delta$ -[(OH)(en)<sub>2</sub>Cr(OH)Cr(en)<sub>2</sub>(OH)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O.<sup>17</sup>

The dimerization reaction of the mono-nuclear complexes to form bridged complexes, *e.g.* diols, has been less studied.<sup>18-19</sup>

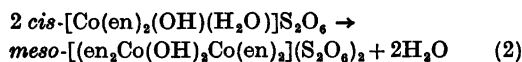
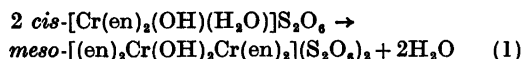
The electronic properties of these bridged systems are of intense current interest. The chromium(III) diols provide simple systems for the study of magnetic interaction between two paramagnetic metal ions.

A super-exchange model  $-JS_A S_B$  ( $J = -450$  cm<sup>-1</sup>) has been used to account for the magnetic susceptibility<sup>20</sup> and the absorption spectra<sup>21,22</sup> of the related system basic Rhodo, [(NH<sub>3</sub>)<sub>4</sub>Cr-O-Cr(NH<sub>3</sub>)<sub>4</sub>]<sup>4+</sup>. This model, which predicts a Landé interval rule to apply to the  $S = 0, 1, 2$ , and 3 levels of the two combined  $S = \frac{3}{2}$  systems is at least for the system in question equivalent to the results of the Angular Overlap Model.<sup>21</sup> However, because of the high energy of the  $S = 2$  and  $S = 3$  levels, their positions have not been established very accurately experimentally. The chromium(III) diol is known to have a weaker magnetic interaction between its two metal ions than have the basic Rhodo. Therefore the  $S = 2$  and  $S = 3$  levels should be easier to reach and possibly directly observable in electron spin resonance. The present mixed diol should prove an important help in interpreting the ESR spectra of the chromium(III) diol, since it provides the best possible model

system for a chromium(III) ion without magnetic interaction and yet with much the same chemical site as in the chromium(III) diol.

## RESULTS AND DISCUSSION

It is a long time since Dubsy<sup>1</sup> and Werner<sup>4</sup> showed that di- $\mu$ -hydroxo binuclear complexes of chromium(III) and cobalt(III), so-called diols, are obtained nearly quantitatively from their parent mono-nuclear species by heating of the solid aquahydroxo dithionates, e.g.



It has recently been shown<sup>7,8</sup> that the diols obtained by these reactions are the *meso* isomers. Similarly the corresponding bis(tetra-amine) diols are obtained by heating of the solid sulfates<sup>1,2</sup> or dithionates<sup>8</sup> of their parent mono-nuclear aquahydroxo species. The method seems to be quite general and has been applied on several other diamine complexes.

In our preliminary attempts to prepare a mixed diol,  $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2]^{4+}$ , we therefore used the above method and as starting material used the cocrystallized dithionates of *cis*- $[\text{Cr}(\text{en})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$  and *cis*- $[\text{Co}(\text{en})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$ . As expected we obtained a mixture of the *meso* isomers of chromium(III) diol, cobalt(III) diol and mixed diol. The formation of mixed diol we could show unambiguously, but its isolation as a pure salt we never achieved.

The method which finally led to the isolation of pure mixed diol is based firstly on a modification of the above procedure so as to give mixed

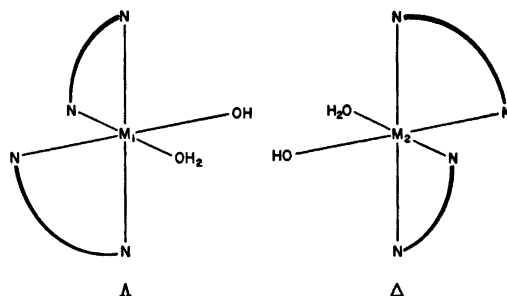


Fig. 1. Assumed packing of the cations in the dithionate of *cis*- $[\text{M}(\text{en})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$  ion. A.  $\text{M}_1 = \text{M}_2 = \text{Cr}(\text{III})$  (or  $\text{Co}(\text{III})$ ); mono-nuclear species condense so as to give *meso* chromium(III) diol (or *meso* cobalt(III) diol) as shown recently.<sup>7,8</sup> B.  $\text{M}_1 = \text{Cr}$  and  $\text{M}_2 = \text{Co}$ ; mono-nuclear species condense so as to give  $(-)\text{-}\Delta\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2]^{4+}$  as described in the text.

diol nearly quantitatively and with only a small contamination of the chromium(III) and cobalt(III) diols and secondly on a kinetically controlled fractionation procedure.

It was assumed that the formation of *meso* diols in the reactions (1) and (2) is facilitated by the packing of the cations in the dithionate, i.e. pairwise packing of cations of opposite chirality, oriented much as shown in Fig. 1. This would explain why *meso* diol rather than *racemic* diol is formed. It is then likely that the cocrystallized dithionates of  $\Delta$ -*cis*- $[\text{Cr}(\text{en})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$  and  $\Delta$ -*cis*- $[\text{Co}(\text{en})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$ , if they form an active racemate, will pack also as shown in Fig. 1 and therefore by heating will form mainly the optically active mixed diol,  $\Delta, \Delta$ - $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2]^{4+}$ . Our experiments, based upon these hypotheses, have been successful, and the crude perchlorate salt obtained

Table 1. Analytical data for the different fractions of the mixed diol.

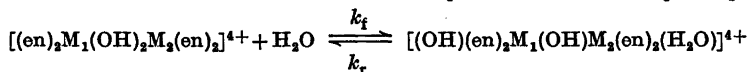
	% Cr 6.64 <sup>a</sup>	% Co 7.53 <sup>a</sup>	% chromium(III) diol <sup>b</sup>	% cobalt(III) diol <sup>c</sup>
Crude perchlorate	6.45	7.70	1.3	4.0
Fraction F <sub>c1</sub>	6.65	7.51	0.2	0.2
Fraction F <sub>c2</sub>	6.67	7.50	0.8	0.5
Fraction F <sub>c3</sub>	6.66	7.50	1.2	1.0

<sup>a</sup> Calculated for  $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2](\text{ClO}_4)_4$ . <sup>b</sup> Calculated from ESR measurements. <sup>c</sup> Upper limit for the contamination with cobalt(III) diol, calculated on the basis of an estimated error ( $\pm 0.01$ ) on the metal analyses.

Table 2. Kinetic and thermodynamic properties of mono-ols and diols.<sup>a</sup>

	$10^3 k_f$ min <sup>-1</sup>	20°C $10^3 k_r$ min <sup>-1</sup>	$K_{eq}$	$10^3 k_f$ min <sup>-1</sup>	0.8°C $10^3 k_r$ min <sup>-1</sup>	$K_{eq}$	Ref.
(-) <sub>889</sub> -A, A-[(en) <sub>2</sub> Cr(OH) <sub>2</sub> Co(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>4</sub>	24	6	4 ± 1	2.4	0.6	4 ± 1	23 <sup>b</sup>
meso-[(en) <sub>2</sub> Cr(OH) <sub>2</sub> Cr(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>4</sub>	23.5	30.8	0.76	2.21	2.54	0.84	15,16

<sup>a</sup> All data refer to the medium 1 M NaClO<sub>4</sub>. The rate constants  $k_f$  and  $k_r$  refer to the equilibration reaction



where M<sub>1</sub> and M<sub>2</sub> can both be Cr or Co so that  $k_f$  and  $k_r$  refer to composite terms as shown in Ref. 23.

<sup>b</sup> Calculated from the data given in the reference.  $K_{eq} = [\text{aquahydroxo mono-ol}]/[\text{diol}]$ .

by this method is seen (Table 1) to be nearly pure. The small contamination with chromium(III) diol and cobalt(III) diol is almost certainly due to contamination with racemic aquahydroxo dithionates contained in the starting material, {A-cis-[Cr(en)<sub>2</sub>(OH)(H<sub>2</sub>O)], A-cis-[Co(en)<sub>2</sub>(OH)(H<sub>2</sub>O)]}(S<sub>2</sub>O<sub>6</sub>)<sub>2</sub>.

Pure mixed diol (99.6 % pure, see Table 1) was then obtained by a kinetically controlled fractionation procedure. This procedure takes advantage of the fact that the kinetics and thermodynamics of the mono-ol/diol systems are different for the three cases, Cr diol, mixed diol, and Co diol. The first two systems enter rather rapidly into equilibrium with their respective mono-ols, but with somewhat different rates and equilibrium constants<sup>23</sup> as shown in Table 2. The cobalt(III) diol's behaviour in this respect is still an unsolved problem. However, important in this connection is the fact that neutral or slightly acid [ $[H^+] \leq 10^{-3}$  M] solutions of the cobalt(III) diol after hours at room temperature do not contain any significant amounts of mono-ol and by addition of sodium perchlorate rapidly gives precipitation of cobalt diol perchlorate nearly quantitatively. The fractionation procedure is based upon these properties as described below. An aqueous solution of the crude mixed diol perchlorate (slightly contaminated with chromium(III) diol and cobalt(III) diol) is allowed to equilibrate with respect to mono-ol/diol. Addition of sodium perchlorate then causes nearly instantaneous precipitation of the diols. Upon further standing the mixture reequilibrates, i.e. aqua-

hydroxo mono-ol is transformed back into diol, which as a perchlorate is much less soluble than the parent mono-ol. However, the reformation of diol is approximately five times faster for the chromium(III) diol than for the mixed diol (see  $k_r$  values in Table 2). Therefore, removal of the precipitate at the time where re-formation and precipitation of chromium(III) diol is essentially complete, gives a solution from which pure mixed diol precipitates (fraction F<sub>c1</sub>, see Table 1). From the first and impure fraction (F<sub>a1</sub>) further two fractions (F<sub>c2</sub> and F<sub>c3</sub>) were obtained by repeating the kinetically controlled fractionation procedure. These fractions, however, are not as pure as F<sub>c1</sub>. Obviously the fractionation procedure only gives a very pure product if the contamination with chromium(III) diol is relatively small.

Evidence that the compound actually is a mixed diol is provided in the following.

The compound was analyzed as [CrCo(en)<sub>4</sub>(OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> which strongly indicated a polynuclear structure with no terminal OH or OH<sub>2</sub> groups. The likely possibility that the compound was an equimolar mixture of chromium(III) diol and cobalt(III) diol could be excluded unambiguously from its absorption spectra (data in Table 3). The compound has no terminal OH<sup>-</sup> groups as shown by the visible absorption spectra (at 0 °C and extrapolated back to the time of dissolution), which were identical for the two media {10<sup>-3</sup> M HClO<sub>4</sub>, 1 M NaClO<sub>4</sub>} and {1 M HClO<sub>4</sub>} (Table 3). These observations strongly suggest a hydroxo bridged structure. It was then shown that the Guinier powder

Table 3. Spectral data for the three diols at 0.8°C. Medium 0.001 M HClO<sub>4</sub>, 1 M NaClO<sub>4</sub>.

Compound	$(\epsilon, \lambda)_{\max}$	
$(-)\text{meso-}A, A\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2](\text{ClO}_4)_4$	(229, 528) <sup>a</sup>	(149, 383) <sup>a</sup>
	(231, 528)	(148, 383)
$A, A\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2](\text{ClO}_4)_4$	(199, 540) <sup>b</sup>	(107, 386) <sup>b</sup>
$A, A\text{-}[(\text{en})_2\text{Co}(\text{OH})_2\text{Co}(\text{en})_2](\text{ClO}_4)_4$	(298, 525)	(242, 375) sh

<sup>a</sup> Medium 1 M HClO<sub>4</sub>. <sup>b</sup> Taken from Ref. 16.

diffraction pattern of the perchlorate of the compound is nearly identical to that of *meso*-[(en)<sub>2</sub>Cr(OH)<sub>2</sub>Cr(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> whose cation's structure is known.<sup>7</sup> Also the patterns of the corresponding two dithionates show great similarities. This is evidence that the nuclearity of the mixed diol is two and that the chiralities of the two units building up its binuclear cation are opposite. The cation [(en)<sub>2</sub>Cr(OH)<sub>2</sub>Co(en)<sub>2</sub>]<sup>4+</sup> comprises four chiral isomers, *AA*, *ΔΔ*, *ΛΛ*, and *ΔΛ*, making up two catoptric (enantiomeric) pairs. The present *meso* mixed diol *ACrΔCo* is an internal active racemate which owes its chirality to the lack of intramolecular configurational cancelling caused by the fact that the two central ions are different. As expected the compound showed optical rotation, and the fact that the rotation did not change upon reprecipitation is evidence that the compound is a pure isomer. From the configuration<sup>24,25</sup> of the parent species used as starting materials we therefore find it most certain that the configuration is *A* around the chromium(III) ion and *A* around the cobalt(III) ion.

The results given above do not exclude the possibility that the compound is contaminated with small amounts of chromium(III) diol and cobalt(III) diol in the ratio 1:1. Such a contamination does not alter the elemental analyses and only to a negligible extent affect the other measurements quoted above. ESR spectroscopy, however, provides an excellent tool for the solution of this problem. As shown in Fig. 2 the ESR spectrum of the chromium(III) diol is very complex compared to its corresponding mononuclear species, *cis*-[Cr(en)<sub>2</sub>(OH)<sub>2</sub>]<sup>+</sup>. This difference is caused by interaction between the two paramagnetic chromium(III) ions in the diol. In the mixed diol such an interaction would not have much consequence and the

ESR spectrum is therefore very similar to that of the parent mononuclear chromium(III) species as shown in Fig. 2. The cobalt(III) diol and the cobalt(III) nucleus in the mixed diol are both diamagnetic and therefore do not give an ESR spectrum. The mixed diol is clearly

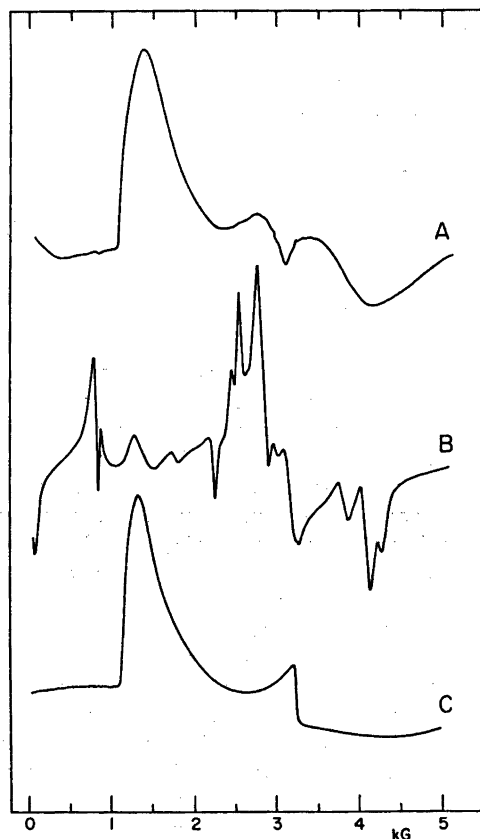


Fig. 2. ESR spectra at -140°C in glycerol-water (1:1) glass of the cations  $(-)\text{meso-}A, A\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2]^{4+}$  (A),  $A, A\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2]^{4+}$  (B), and *cis*-[Cr(en)<sub>2</sub>(OH)<sub>2</sub>]<sup>+</sup> (C).

seen to be almost pure with respect to contamination with chromium(III) diol. The small peak at 0.85 kG, however, was shown to be due to such a contamination. Furthermore, from measurements on samples of the mixed diol artificially contaminated with the chromium-(III) diol (up to 5 %) it was shown that the peak height at 0.85 kG relative to the peak height at 1.4 kG can be used as a reliable quantitative measure of the contamination with chromium(III) diol. The results of such an analysis are given in Table 1.

## EXPERIMENTAL

**Materials.** Ammonium bromocamphorsulfonate ( $[\alpha]_{589}^{20} = 85^\circ$  for 2 % aqueous solution) was obtained from bromocamphor.<sup>28</sup> *cis*-[Co(en)<sub>2</sub>Cl(H<sub>2</sub>O)]SO<sub>4</sub>·2H<sub>2</sub>O was obtained from [Co(en)<sub>2</sub>CO<sub>3</sub>]Cl<sup>27</sup> and then converted to the chloride by treatment with 12 M hydrochloric acid at 0 °C. The resolution of the latter salt into its (-)<sub>589</sub>-*A* and (+)<sub>589</sub>-*A* isomers was effected by the method of Werner.<sup>28</sup> The (-)<sub>589</sub>-*A* isomer was converted to (-)<sub>589</sub>-*A*-[Co(en)<sub>2</sub>CO<sub>3</sub>]I as described by Dwyer, Sargeson and Reid.<sup>29</sup> (+)<sub>589</sub>-*A*-*cis*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O was isolated from racemic<sup>30</sup> *cis*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O through its bromocamphorsulfonate by a modification of methods previously described.<sup>31,32</sup> The method given here has the advantage that the yield based on the rather expensive ammonium bromocamphorsulfonate has been considerably increased. The *meso*-[(en)<sub>2</sub>Cr(OH)<sub>2</sub>Cr(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>, *meso*-[(en)<sub>2</sub>Co(OH)<sub>2</sub>Co(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> and *cis*-[Cr(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Br<sub>2</sub>·2H<sub>2</sub>O were synthesized as published elsewhere.<sup>8</sup> All other chemicals were analytical grade.

**Analysis.** Chromium and cobalt analysis determined by atomic absorption spectrophotometry was performed by K. Jørgensen, Chemistry Department I, H. C. Ørsted Institute, and C, N, H, and Cl analyses were made by the microanalytical laboratory at the H. C. Ørsted Institute, Copenhagen.

**Instruments.** A Zeiss DMR 21 spectrophotometer was used for all spectrophotometric measurements in the visible region. For the spectrophotometric data given below the absorbancy  $\epsilon$  has been given in l mol<sup>-1</sup> cm<sup>-1</sup> and the wavelength  $\lambda$  has been given in nm. The molarity of solutions of the dimers was always defined as the number of mol of dimer and not the number of mol of chromium(III) per litre of solution. The optical rotations were measured on a Perkin Elmer Model 141 polarimeter. Guinier powder diffraction diagrams were measured with a Guinier powder camera with CuK $\alpha_1$  radiation. ESR spectra were recorded at 9.111 GHz on a JEOL JES-ME-1X spectrometer.

**Preparative procedures.** 1. (+)<sub>589</sub>-*A*-*cis*-Di-chlorobis(ethylenediamine)chromium(III) chloride monohydrate. (+)<sub>589</sub>-*A*-*cis*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O. To a freshly prepared (within 2 min) solution of *cis*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O (60.0 g, 0.202 mol) in water (1 l) at 20 °C was added ammonium bromocamphorsulfonate (40.0 g, 0.122 mol) within 5 min and under vigorous stirring. Precipitation of the diastereoisomer commenced during the addition of the ammonium bromocamphorsulfonate and after further 5 min the precipitate was filtered off, washed with 96 % ethanol and then with ether. Drying in air yielded 32 g. This was dissolved in ice-cold 12 M hydrochloric acid (130 ml) and with stirring and cooling in ice added cold 96 % ethanol (260 ml). After 5 min the precipitate was filtered off and washed with 96 % ethanol and then with dry ether. Drying in air yielded 16.5 g of (+)<sub>589</sub>-*A*-*cis*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O (46 % based on ammonium bromocamphorsulfonate). The rotation ( $[\alpha]_{589}^{25} = 268 \pm 3^\circ$  for 0.075 % aqueous solutions) was unchanged upon further reprecipitation with 96 % ethanol from 12 M hydrochloric acid ( $[\alpha]_{589}^{25} = 271^\circ$ ) or by repeated reprecipitation with ammonium bromocamphorsulfonate ( $[\alpha]_{589}^{25} = 268^\circ$ ).

2. Cocrystallized dithionate of *A*-*cis*-aquabis(ethylenediamine)hydroxochromium(III) and *A*-*cis*-aquabis(ethylenediamine)hydroxocobalt(III) cations. {*A*-*cis*-[Cr(en)<sub>2</sub>(OH)(H<sub>2</sub>O)]}, *A*-*cis*-[Co(en)<sub>2</sub>(OH)(H<sub>2</sub>O)](S<sub>2</sub>O<sub>6</sub>)<sub>2</sub>. *A*-(-)<sub>589</sub>-[Co(en)<sub>2</sub>CO<sub>3</sub>]I (22 g, 60 mmol) was dissolved in 1 M nitric acid (130 ml) at 0 °C within 12 min. Then solid silver nitrate (44.2 g, 260 mmol) and *A*-(+)<sub>589</sub>-*cis*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O (17.8 g, 60 mmol) was added and the mixture thoroughly stirred for 10 min. The silver halides were filtered off and to the filtered solution was added, with stirring and cooling in ice, a solution of sodium dithionate dihydrate (40 g, 165 mmol) in water (180 ml, 20 °C). Then pyridine (160 ml, 0 °C) was added and precipitation of the active racemic mixed dithionate of the aquahydroxo complexes commenced within 5 s. After further 50 s the precipitate was filtered off and washed twice with water (40 ml), three times with 96 % ethanol (80 ml), and then thoroughly dried with ether. Drying in air yielded 21.8 g (49 %) of {*A*-*cis*-[Cr(en)<sub>2</sub>(OH)(H<sub>2</sub>O)]}, *A*-*cis*-[Co(en)<sub>2</sub>(OH)(H<sub>2</sub>O)](S<sub>2</sub>O<sub>6</sub>)<sub>2</sub>.

3. (-)<sub>589</sub>-Di- $\mu$ -hydroxo-*A*-bis(ethylenediamine)chromium(III)-*A*-bis(ethylenediamine)cobalt(III) perchlorate. (-)<sub>589</sub>-*A*, *A*-[(en)<sub>2</sub>Cr(OH)<sub>2</sub>Co(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>. The crude {*A*-*cis*-[Cr(en)<sub>2</sub>(OH)(H<sub>2</sub>O)]}, *A*-*cis*-[Co(en)<sub>2</sub>(OH)(H<sub>2</sub>O)](S<sub>2</sub>O<sub>6</sub>)<sub>2</sub> (21.8 g, 0.0294 f.w.) was added to acetic acid anhydride (220 ml). The suspension was heated to reflux within 20 min, kept at reflux for another 30 min and then cooled in an ice bath. The sample was filtered and washed twice with 96 % ethanol (100 ml), twice with 2 M acetic acid (100 ml), three times with 96 % ethanol (100 ml), and finally thoroughly with ether. By the washing with acetic acid, a

small amount of unreacted *cis*-aqua-hydroxo monomer is removed.\* Drying in air yielded 20.3 g (98 %) of crude  $(-)\text{S}_{599}\text{-}A, A\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2](\text{S}_2\text{O}_8)_3$ . This crude dithionate was then added to a saturated solution of ammonium bromide (90 ml) and the suspension was kept at room temperature with stirring for 1 h. The purple crystals of the bromide were filtered off and treated once more with ammonium bromide (45 ml) for half an hour. The sample was filtered and washed with 50 % v/v ethanol (50 ml), twice with 96 % ethanol (50 ml), and then with ether. Drying in the air yielded 20.8 g (95 % based on the dithionate of the aquahydroxo complexes) of crude  $(-)\text{S}_{599}\text{-}A, A\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2]\text{Br}_4 \cdot 2\text{H}_2\text{O}$ . The crude bromide (20.8 g, 28 mmol) was then added to a mixture of a saturated solution of sodium perchlorate (150 ml) and water (150 ml), and the suspension was stirred at room temperature for 1 h. The violet crystals of the perchlorate were collected on a filter, washed with 50 % v/v ethanol (40 ml), twice with 96 % ethanol (80 ml), and thoroughly washed with ether. Drying in air yielded 19.7 g (86 % based on the dithionate of the aquahydroxo complexes) of nearly pure  $(-)\text{S}_{599}\text{-}A, A\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2](\text{ClO}_4)_4$  (see Table 1).

**Fractionation procedure.** Pure mixed diol was obtained by fractional reprecipitation of the above crude perchlorate. As the following fractionation procedure is kinetically controlled the procedure given below must be followed strictly in order to get a successful result.

The crude mixed diol perchlorate (19.0 g, 24.3 mmol) was dissolved in  $10^{-3}$  M  $\text{HClO}_4$  (270 ml) at 20.0 °C and kept at that temperature for 17 min. Then a saturated solution of sodium perchlorate (270 ml, 20.0 °C) was added with stirring and precipitation of diol perchlorate commenced within a few seconds. After further 9 min at 20.0 °C, with continued stirring, the sample was filtered off within 20 s, washed with 96 % ethanol and then ether. Drying in air yielded 10.6 g (55.8 %) of fraction  $F_{a1}$ . The mother liquor was left at 20.0 °C with stirring for 1 h. During this time the precipitation of diol perchlorate became essentially complete. The precipitate was isolated as above to give 4.40 g (23 %) of fraction  $F_{b1}$ . Kinetically controlled fractional reprecipitation of  $F_{a1}$  (10.6 g) as above yielded 5.9 g (56 %) of fraction  $F_{a2}$  and 2.25 g (21 %) of fraction  $F_{b2}$ . Finally, fractional reprecipitation of  $F_{a2}$  (5.90 g) yielded 3.40 g (58 %) of fraction  $F_{a3}$  and 0.99 g (16.8 %) of fraction  $F_{b3}$ .

The  $F_b$  fractions were reprecipitated in the following way. The diol perchlorate (1.00 g) was dissolved in  $10^{-3}$  M perchloric acid (20 ml, 0 °C) and to the filtered solution was added a saturated solution of sodium perchlorate (20 ml,

20 °C) with stirring and cooling in ice. These operations were performed within 20 s in order to avoid formation of mono-ol. Precipitation of diol perchlorate commenced almost instantaneously. After 3 min the sample was filtered off and washed with 96 % ethanol and then ether. Drying in air yielded  $0.80 \pm 0.02$  g (80 %) of pure  $(-)\text{S}_{599}\text{-}A, A\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2](\text{ClO}_4)_4$ , fractions  $F_{c1}$ ,  $F_{c2}$ , and  $F_{c3}$ , respectively. The yields of these pure or nearly pure (see below) fractions based on  $\{A\text{-}cis\text{-}[\text{Cr}(\text{en})_2(\text{OH})(\text{H}_2\text{O})], A\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{OH})(\text{H}_2\text{O})]\}(\text{S}_2\text{O}_8)_2$  were 16 % ( $F_{c1}$ ), 8.1 % ( $F_{c2}$ ), and 3.6 % ( $F_{c3}$ ).

**Purity of the fractions and some properties of the mixed diol.** The  $F_{c1}$  fraction analyzed as pure mixed diol. Anal. calc. for  $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2](\text{ClO}_4)_4$ : C 12.27; N 14.31; Cl 18.11; H 4.38. Found: C 12.22; N 14.42; Cl 17.98; H 4.47. Metal analyses for the different fractions are collected in Table 1. The visible absorption spectra changed with time due to formation of mono-ol. However, when measured at 0 °C and with short intervals (2 and 5 min, respectively) after the time of dissolution  $t_0$  the absorptivity  $\epsilon$  could be extrapolated linearly back to  $t_0$ . These extrapolated spectra were nearly identical for the three  $F_c$  fractions. In Table 3  $(\epsilon, \lambda)_{\text{max}}$  values for the  $F_{c1}$  fraction are given.

Correspondingly the ESR spectra of the chromium(III) diol and the mixed diol, used for the calculations given in Table 1, and shown in Fig. 2, were taken on freshly prepared solutions. Diol perchlorate was dissolved in  $10^{-3}$  M  $\text{HClO}_4$  (0 °C) and added one volume of glycerol (0 °C) within 1 min, and then rapidly frozen. The contents of mono-ol in these solutions were therefore negligible. The ESR spectrum of *cis*- $[\text{Cr}(\text{en})_2(\text{OH})_2]^+$  was measured on a glass of *cis*- $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2]\text{Br}_3 \cdot 2\text{H}_2\text{O}$  in a 1:1 mixture of 0.1 M NaOH (aqueous) and glycerol. The optical rotations,  $[\alpha]_{599}^{30}$ , of freshly prepared solutions changed rapidly with time and became nearly constant after 12 min. Values of  $[\alpha]_{599}^{30}$  for the time of dissolution,  $\alpha_0$ , and for the time where constant readings were measured,  $\alpha_\infty$ , were obtained from plots of  $\log(\alpha_t - \alpha_\infty)$  against time,  $t$ . The three  $F_b$  and the three  $F_c$  fractions showed all nearly identical values for both  $\alpha_0 = -214 \pm 4^\circ$  and  $\alpha_\infty = -102 \pm 2^\circ$  (0.1 % solutions in  $10^{-3}$  M  $\text{HClO}_4$ , 1 M  $\text{NaClO}_4$ ). The observed variations in the  $\alpha_0$  and the  $\alpha_\infty$  values were not systematic and mainly due to errors in the measurements.

The Guinier powder X-ray diffraction diagram of  $(-)\text{S}_{599}\text{-}A, A\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2](\text{ClO}_4)_4$  was nearly identical to that of *meso*- $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2](\text{ClO}_4)_4$ . A similar identity was found between the corresponding two dithionates. Pure *A, A*- $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2](\text{S}_2\text{O}_8)_2$  was obtained by adding a solution of sodium dithionate to a freshly prepared solution at 0 °C of the perchlorate. Thereby  $(-)\text{S}_{599}\text{-}A, A\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2](\text{S}_2\text{O}_8)_2$  precipitated nearly in-

\* It should be noted that mixing of the mother liquor with ethanol is not advisable because of the possibility of a vigorous formation of ethyl acetate.

stantaneously. The salt was not further characterized.

*Acknowledgement.* The present work was written whilst we were both Visiting Fellows at the Australian National University. We take this opportunity to thank the Research School of Chemistry for support and for excellent working facilities. Grants from Statens Naturvidenskabelige Forskningsråd are further acknowledged.

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Received May 19, 1976.

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