

# New Hydroxo-bridged Polynuclear Ethylenediamine Chromium(III) Complexes

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

New polynuclear  $\mu$ -hydroxo ethylenediamine chromium(III) complexes have been isolated and identified. Together with mononuclear complexes they were found in aqueous ethylenediamine (=en) buffer solutions with  $C_{Cr(III)}=0.1$  M,  $C_{en, 2HCl}=0.3$  M, and  $pH \approx 8$ , in which equilibrium between the mononuclear species was established by the catalytic effect of chromium(II)+charcoal at room temperature. The same polynuclear complexes were also found in similar solutions kept at 40–50 °C for 3–5 days.

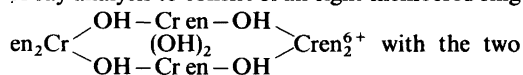
Crystalline salts of  $en_2Cr(OH)_2Cr(en)(OH)_2Cr(en)_2^5+$  and of three tetranuclear complexes with the formula  $Cr_4en_6(OH)_6^+$ , viz. one of unknown structure (b1), the racemic complex  $\Delta\{\Delta\Lambda\Lambda\}/\Lambda\{\Lambda\Delta\Delta\}-Cr\{(OH)_2Cr(en)_2\}_3^+$  (b2) (i.e. the analogue of Werner's brown salt) and the centrosymmetric  $\Delta\Delta\Delta\Lambda$ - $lel_6-en_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2^6+$  (b3), were isolated. The salts were isolated by ion-exchange chromatography followed by precipitation as iodides and purification by fractional crystallization from water–ethanol mixtures.

The identification was based primarily on the following observations: Hydrolysis of these and other hydroxo-bridged Cr(III)-en complexes with 70% perchloric acid gave the corresponding mononuclear aquaamines quantitatively as shown by, e.g., ESR spectroscopy. X-Ray diffraction patterns of powders and single crystals of salts of b2 confirmed the proposed structure by their similarity to the patterns for corresponding cobalt salts of known structure, and a single crystal X-ray structure analysis of the bromide dihydrate (tetrahydrate) of b3 provided the structural details for

this compound. The latter crystallizes in the monoclinic space group  $P2_1/n$  with  $a=15.45_0$  Å,  $b=16.42_0$  Å,  $c=7.95_2$  Å,  $\beta=99.3_6^\circ$ , and  $Z=2$ . Final refinement of 3319 diffractometer reflections (MoK $\alpha$  radiation) led to  $R=0.044$  and  $R_w=0.048$ .

Remarkably few polynuclear chromium(III) complexes have been isolated considering the enormous amount of work that has been devoted to mononuclear species, and considering the fact that the dominant species present in aqueous solutions of chromium(III) under appropriate conditions are polynuclear.

In the case of hydroxo-bridged ethylenediamine (=en) chromium(III) complexes only a few have been isolated. The dinuclear  $en_2Cr(OH)_2Cr(en)_2^{4+}$  (often called the diol) and its open form,  $(H_2O)en_2Cr(OH)Cr(en)_2(OH)^{4+}$ , are known in the  $\Delta\Lambda$  (*meso*)<sup>2</sup> as well as in the  $\Delta\Delta/\Lambda\Lambda$  (racemic)<sup>3</sup> form. The rhodoso,  $Cr_4en_6(OH)_6^+$ , has been shown by X-ray analysis to consist of an eight-membered ring



bis(ethylenediamine)chromium(III) moieties having  $\Delta$  and  $\Lambda$  configuration, respectively.<sup>4</sup> Analogues of the diol and the rhodoso with ammonia are also known.<sup>5–7</sup>

In an investigation of equilibria in aqueous solution between chromium(III) and ethylenediamine<sup>8</sup> we observed several bands containing polynuclear species during ion-exchange chromatography of the equilibrium mixtures. However, it is difficult to

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crystallize salts of these usually highly charged molecules when they constitute only a minor fraction of the products in solution, and such difficulties may be partly responsible for the small number of polynuclear chromium(III) complexes which are known. In order to throw more light on the condensation of chromium(III) we decided to investigate some of the ion-exchange bands containing polynuclear complexes in the hope of finding sufficiently few species in these bands to make crystallization feasible.

## EXPERIMENTAL

*Chromium(III)-en solutions.* The basis for the work is the chromium(II)+charcoal catalyzed solutions described elsewhere.<sup>8</sup> For preparative purposes we used solutions with higher  $C_{Cr}$  ( $\approx 0.1$  M) and  $\text{pH} \approx 8$ , and instead of catalysis at room temperature we simply kept the solutions at 40–50 °C for 3–5 days uncatalyzed. This resulted in solutions with almost the same composition of complexes as similar catalyzed ones. The procedure below for the separation and precipitation made use of solutions prepared in the following way:

26 g [ $\text{Cren}_3$ ] $\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ , 20 g en.2HCl, and 1.5 g en (anhydrous) were dissolved in water to 500 ml. This solution with  $C_{Cr} = 0.13$  M was kept at 40–50 °C for 3–5 days, and then cooled to room temperature and its components were separated in the course of the next few days.

*Ion-exchange separation.* This and the following sections should be read in conjunction with Table 1, which gives a survey of the contents of the different bands.

50 ml of the chromium solution were diluted  $\times 10$  with ice-cold water and passed down a column of Sephadex SP-C25 (2 cm  $\times$  7 cm  $\varnothing$ ). A part of the mononuclear complexes was removed in this way. The chromium-containing resin was then

transferred to the top of another column of Sephadex SP-C25 (15–20 cm  $\times$  2.5 cm  $\varnothing$ ) and eluted with 0.7 M NaCl. In this way we isolated two bands: (a) A rather well-defined violet band directly following the mononuclear bands, the slowest of which contained the yellow  $\text{Cren}_3^{3+}$ . As this violet a-band left the column it was diluted  $\times 10$  with water (0 °C) and concentrated on another column of Sephadex SP-C25 (2 cm  $\times$  2.5 cm  $\varnothing$ ). (b) The a-band was followed by a red-brown b-band, which was less well separated from the subsequent violet bands. When this b-band reached the bottom of the column the dark violet top of the column was replaced by a 1 cm layer of pure Sephadex SP-C25 and the b-band eluted further with more concentrated eluent (see below).

*Precipitation of crude iodides.* The columns containing the isolated bands, a and b, were washed with water and then eluted slowly with 2 M NaI. The most concentrated portions of the eluates (15–20 ml) were allowed to stand at room temperature for 1–2 h (some more solid NaI was added when necessary) after which the precipitates formed were washed with a little 2 M NaI and then washed free of NaI with ethanol. Yields: 70 mg iodide from the a-band and 130 mg iodide from the b-band, corresponding to 3% and 5%, respectively.

*Precipitation of pure salts from the crude iodides.* (a) 100 mg of the crude iodide from the a-band were mixed with 1.0 ml 70% ethanol + 0.40 g  $\text{LiNO}_3$  and the mixture was allowed to stand overnight at room temperature. The precipitate was washed free of  $\text{LiNO}_3$  with ethanol. Yield: 65 mg crude nitrate containing iodide. The 65 mg crude nitrate were dissolved in 5.0 ml 70% ethanol after which 1.0 g  $\text{LiNO}_3$  was added. After a day at room temperature thin violet crystal plates of a nitrate were isolated and washed with ethanol. Yield: 50 mg (74%). The product contained traces of iodide, which were removed by a further recrystallization by the same procedure, with a loss of 15%.

Table 1. Summary of the content of the different bands from ion-exchange separation of a typical chromium(III)-en solution, Cr(II)+charcoal catalyzed or heat-treated, with  $C_{Cr} = 0.1$  M,  $C_{\text{en}, 2\text{HCl}} = 0.3$  M and  $\text{pH} \approx 8$ .

Band	Cr <sup>a</sup> (mol %)	Isolated complexes
First	5–10	Mainly mononuclear species such as $\text{Cr en}_2(\text{OH})_2^+$ and $\text{Cr en}_3^{3+}$ <sup>8</sup>
a	11–12	a, $\text{en}_2\text{Cr}(\text{OH})_2\text{Cr en}(\text{OH})_2\text{Cr en}_2^{5+}$
b	16–17	b1, $\text{Cr}_4\text{en}_6(\text{OH})_6^{6+}$ (from fraction bI) b2, $\text{Cr}\{(\text{OH})_2\text{Cr en}_2\}_3^+$ (from fractions bI and bII) b3, $\text{en}_2\text{Cr}(\text{OH})_2\text{Cr en}(\text{OH})_2\text{Cr en}(\text{OH})_2\text{Cr en}_2^{6+}$ (from fraction bIII)
Last	63–65	

<sup>a</sup> Cr content in the bands relative to total Cr content.

( $\beta$ ) 200 mg of the crude iodide from the b-band were extracted with 2 ml portions of water at room temperature and reprecipitated with solid NaI to give the following three crystal powder fractions:

bI, 40 mg blue-violet iodide from the first two extracts.

bII, 80 mg violet iodide from the next 2–3 extracts.

bIII, 30 mg blue-violet iodide from the last 1–2 extracts (which were blue in contrast to the previous which were violet).

100 mg of the bI-fraction were extracted with 1 ml portions of 50% ethanol and each of the first two extracts was treated with *ca.* 100 mg solid  $\text{LiNO}_3$ . Within 0.5 h these two fractions gave violet precipitates which were reprecipitated by dissolving in *ca.* 0.5 ml 50% ethanol and adding a few crystals of solid  $\text{LiNO}_3$ . The red-violet crystal needles were washed with ethanol to give 5–10 mg *bI nitrate*. The subsequent 2–3 extracts gave, after addition of  $\text{LiNO}_3$  to near saturation, *ca.* 20 mg of red-brown thin crystal plates of *b2 nitrate*.

100 mg of the bII-fraction were extracted with 1 ml portions of water and the extracted material was precipitated by addition of an equal volume of ethanol and  $\text{LiNO}_3$  almost to saturation, giving 40–50 mg *b2 nitrate* after washing with ethanol.

The salt was reprecipitated in the same manner.

50 mg of the bIII-fraction were dissolved in 5 ml water at room temperature and solid LiBr was added gradually until precipitation began, the temperature being kept at room temperature. After a couple of hours, when pronounced precipitation had taken place, 5 ml of ethanol were added and the mixture was left overnight. The isolated product was washed with ethanol to give 30 mg of dark violet-blue crystals of *b3 bromide*. The salt was reprecipitated without significant loss by dissolving the 30 mg in 0.5 ml water and adding a little solid LiBr until beginning precipitation. The remaining material in the filtrate from this precipitation could be almost completely precipitated by addition of 0.5 ml ethanol.

( $\gamma$ ) It was possible to prepare salts of a and b1–3 with other anions by metathesis in water/ethanol mixtures with salts such as  $\text{LiNO}_3$ ,  $\text{Li}_2\text{S}_2\text{O}_6$ ,  $\text{LiClO}_4$ , LiBr, and NaI. This generally resulted in crystalline powders. In addition to the above-mentioned nitrates of a, b1, and b2, large crystals of b2 dithionate were obtained by dissolving 5–10 mg of the nitrate in 0.5 ml of a saturated aqueous solution of  $\text{Li}_2\text{S}_2\text{O}_6$  and subsequently adding 2–3 drops of methanol. The crystals formed at room temperature were washed with water (0 °C) and could be recrystallized from a little water at 30–

Table 2. Chemical analyses of some of the salts of a and b1–b3. The numbers in parentheses are values calculated on the basis of the formulae given.

Compound	% Cr	% Halogen	% N (total)	% N (from en)	% C	% H
a $[\text{Cr}_3\text{en}_5(\text{OH})_4](\text{NO}_3)_5 \cdot 2\text{H}_2\text{O}$	17.64 (17.93)		24.07 (24.14)	16.27 (16.09)	14.16 (13.79)	5.50 (5.51)
$[\text{Cr}_3\text{en}_5(\text{OH})_4]1_5 \cdot 6\text{H}_2\text{O}$	12.39 (12.32)	50.28 (50.10)	11.00 (11.05)			
b1 $[\text{Cr}_4\text{en}_6(\text{OH})_6](\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$	18.18 (18.09)		21.78 (21.93)		13.04 (12.52)	5.61 (5.74)
b2 $[\text{Cr}_4\text{en}_6(\text{OH})_6](\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$	18.05 (18.09)		21.90 (21.93)	14.62 (14.62)	12.24 (12.52)	5.62 (5.74)
$[\text{Cr}_4\text{en}_6(\text{OH})_6]1_6 \cdot 6\text{H}_2\text{O}$	13.60 (13.51)	49.48 (49.45)	10.93 (10.92)			
b3 $[\text{Cr}_4\text{en}_6(\text{OH})_6](\text{NO}_3)_6 \cdot 3\text{H}_2\text{O}$	19.11 (18.98)		23.21 (23.01)	15.26 (15.34)		
$[\text{Cr}_4\text{en}_6(\text{OH})_6]\text{Br}_6 \cdot 4\text{H}_2\text{O}^a$	17.08 (17.03)	39.29 (39.25)	13.80 (13.76)			

<sup>a</sup> The single crystal X-ray analysis (see later) revealed only two water molecules of crystallization per complex ion (the difference Fourier synthesis did not indicate any major peaks that could be interpreted as corresponding to other oxygen atoms).

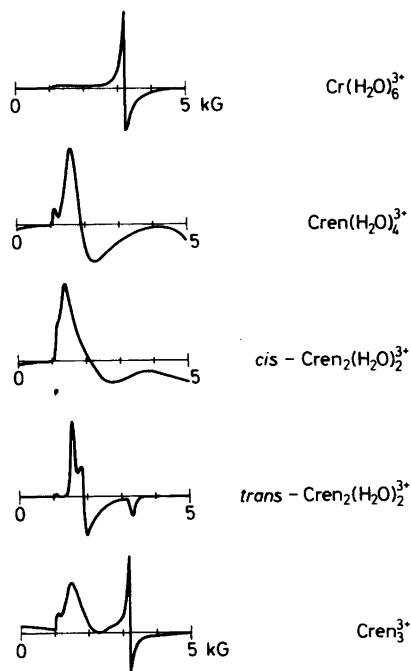


Fig. 1. First derivative ESR spectra at 9.2 GHz of frozen glasses ( $-130^{\circ}\text{C}$ ) of 50% (v/v) glycerol/ $\text{HClO}_4$  solutions of the 3+-charged aquaamines;  $C_{\text{Cr}} = 0.01 - 0.1 \text{ M}$ .

Table 3. The amount of  $\text{Cr en}(\text{H}_2\text{O})_4^{3+}$  relative to the sum of those of  $\text{Cr en}(\text{H}_2\text{O})_4^{3+}$  and  $\text{cis-Cr en}_2(\text{H}_2\text{O})_2^{3+}$  in hydrolyzed polynuclear complexes, as derived from  $b/a$  and Fig. 3.

Hydrolyzed compound	$b/a$	$\text{mol } \frac{0}{0} \text{ Cr en}(\text{H}_2\text{O})_4^{3+}$
Rhodoso perchlorate	3.0 <sub>3</sub>	48
b1 Nitrate	3.2 <sub>0</sub>	52
b3 Nitrate	3.2 <sub>6</sub>	53
a Nitrate	2.5 <sub>5</sub>	35
Diol perchlorate	1.8 <sub>0</sub>	0
b2 Nitrate	1.8 <sub>5</sub>	0

$35^{\circ}\text{C}$ . Large violet-blue crystal plates of b3 nitrate were prepared almost quantitatively by dissolving the bromide or the iodide in water at room temperature followed by precipitation with a little  $\text{LiNO}_3$  and reprecipitation in the same way.

**Chemical analysis.** The prepared compounds were analysed on a microscale (2–5 mg): chromium by atomic absorption spectrophotometry, nitrogen by Kjeldahl, halides by potentiometry, and CHN by usual microtechniques. The results are given in Table 2.

**Hydrolysis with 70% perchloric acid.** 5–10 mg of the crystalline nitrates or perchlorates of six different polynuclear chromium(III) ethylenediamine complexes were treated for 2–5 min at

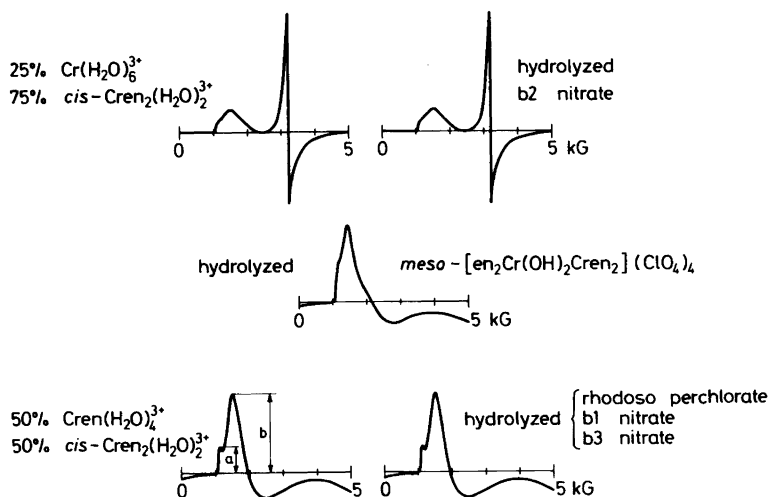


Fig. 2. First derivative ESR spectra (frozen glasses) of mixtures of aquaamines (% = mol %) compared with those of polynuclear salts hydrolyzed at  $70^{\circ}\text{C}$  for *ca.* 5 min with 70% perchloric acid. The ratio between the peak heights  $b$  and  $a$  was used to determine the relative amount of  $\text{Cr en}(\text{H}_2\text{O})_4^{3+}$  in mixtures of  $\text{Cr en}(\text{H}_2\text{O})_4^{3+}$  and  $\text{cis-Cr en}_2(\text{H}_2\text{O})_2^{3+}$  as shown in Fig. 3 and Table 3.

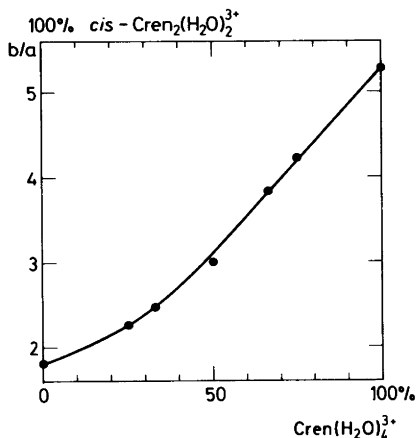


Fig. 3.  $b/a$  (see Fig. 2) as a function of  $100[\text{Cr en}(\text{H}_2\text{O})_4^{3+}]/C_{\text{Cr}}$  ( $C_{\text{Cr}} = [\text{Cr en}(\text{H}_2\text{O})_4^{3+}] + [\text{cis-Cr en}_2(\text{H}_2\text{O})_2^{3+}]$ ). Known amounts of  $\text{Cs}[\text{Cr enCl}_4]$  and  $\text{cis-}[\text{Cr en}_2\text{Cl}_2](\text{ClO}_4)$  were dissolved in 0.5 ml *ca.* 0.5 M  $\text{Hg}(\text{ClO}_4)_2$ , 0.1 M  $\text{HClO}_4$  to give aquaamine solutions with  $C_{\text{Cr}} \approx 0.1$  M. 0.5 ml glycerol was added before freezing to  $-130^\circ\text{C}$ .

$70^\circ\text{C}$  with 0.5 ml 70%  $\text{HClO}_4$  and then cooled in ice. The content of mononuclear complexes after this treatment was determined in two different ways:

(a) The hydrolyzed mixtures were diluted  $\times 1-2$  with glycerol and cooled to  $-130^\circ\text{C}$  within 0.5–1 min to give frozen glasses the ESR spectra of which were measured from 0 to 5 kG at 9.2 GHz. The resulting spectra were compared with similar spectra of glycerol/water glasses containing known amounts of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Cr en}(\text{H}_2\text{O})_4^{3+}$ ,  $\text{cis-Cr en}_2(\text{H}_2\text{O})_2^{3+}$ , and  $\text{trans-Cr en}_2(\text{H}_2\text{O})_2^{3+}$ . The concentration ratios of the species in the former glasses could then be calculated provided that other species were only present in minor amounts. We previously used this procedure successfully to determine the ratio of *cis*- to *trans*- $\text{Cr en}_2(\text{H}_2\text{O})_2^{3+}$ <sup>8</sup> and of *cis*- to *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ .<sup>9</sup> The results are shown in Figs. 1–4 and Table 3.

(b) The hydrolyzed mixtures were diluted  $\times 200$  with water ( $0^\circ\text{C}$ ) and separated on an ion-exchange column of Sephadex SP-C 25 (10 cm  $\times$  1 cm  $\varnothing$ ) with either 0.5 M  $\text{NaClO}_4$  or 0.1 M  $\text{Na}_2\text{SO}_4$ . The  $\text{NaClO}_4$  elution separated 3+ -charged complexes from more highly charged species such as  $\text{CrenenH}(\text{H}_2\text{O})_4^{4+}$  and polynuclear complexes. The  $\text{Na}_2\text{SO}_4$  elution separated  $\text{Cren}(\text{H}_2\text{O})_4^{3+}$  and  $\text{cis-Cren}_2(\text{H}_2\text{O})_2^{3+}$  (the former being eluted faster) provided that the separation was performed with ice-cooled eluent within 0.5–1 h.  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  was separated

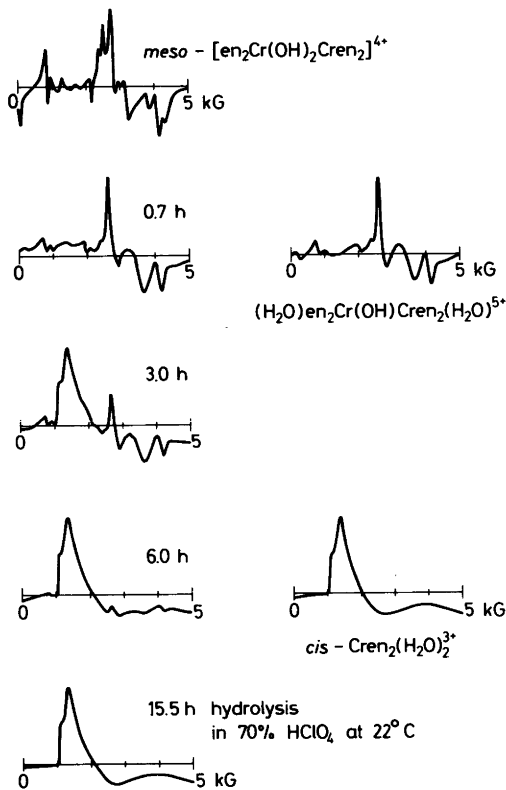


Fig. 4. First derivative ESR spectra (frozen glasses) at different stages of the hydrolysis at room temperature of  $\text{meso-}[\text{en}_2\text{Cr}(\text{OH})_2\text{Cren}_2](\text{ClO}_4)_4$  (left) to be compared with those of  $[(\text{HO})\text{en}_2\text{Cr}(\text{OH})\text{Cren}_2(\text{OH})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  and  $\text{cis-}[\text{Cren}_2(\text{H}_2\text{O})_2]\text{Br}_3 \cdot 2\text{H}_2\text{O}$  in 4 M  $\text{HClO}_4$ .

from  $\text{cis-Cren}_2(\text{H}_2\text{O})_2^{3+}$  on a 1–2 cm  $\times$  1 cm  $\varnothing$  ion-exchange column of Dowex 50 W X8,  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  being eluted with 1.5 M  $\text{H}_2\text{SO}_4$  and subsequently  $\text{cis-Cr en}_2(\text{H}_2\text{O})_2^{3+}$  with 5 M  $\text{H}_2\text{SO}_4$ . The content of chromium complexes in each chromatographic fraction was determined from visible spectra and chromium analyses. The results are given in Table 4.

*Preparation of rhodoso perchlorate and cleavage with 12 M hydrochloric acid.* Rhodoso sulfate,  $[\text{Cr}_4\text{en}_6(\text{OH})_6](\text{SO}_4)_3 \cdot \text{aq}$ , was prepared by a modification<sup>10</sup> of the method of Pfeiffer *et al.*<sup>1</sup>:

150 g  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , 150 ml ethylenediamine, and 250 ml 1-pentanol were heated to  $110^\circ\text{C}$  under stirring for 6–15 h and the mixture then left to cool. After filtration and washing with methanol an orange, crude product consisting mainly of  $[\text{Cr}_4\text{en}_6-$

Table 4. Ion-exchange separations of polynuclear compounds hydrolyzed with 70 % HClO<sub>4</sub> at 70 °C for 2–5 min.

Hydrolyzed compound	Eluent	% Chromium relative to total chromium content	
		1st Band	2nd Band
Rhodoso perchlorate on Sephadex SP-C25	0.5 M NaClO <sub>4</sub>	101 <sup>a</sup>	
	0.1 M Na <sub>2</sub> SO <sub>4</sub>	54 <sup>c</sup>	47 <sup>d</sup>
b2 Nitrate on Dowex 50 W X8	1.5 M H <sub>2</sub> SO <sub>4</sub> then	23 <sup>e</sup>	
	5 M H <sub>2</sub> SO <sub>4</sub>		75
b3 Nitrate on Sephadex SP-C25	0.5 M NaClO <sub>4</sub>	96 <sup>a</sup>	
	0.1 M Na <sub>2</sub> SO <sub>4</sub>	50 <sup>c</sup>	47 <sup>d</sup>
a Nitrate on Sephadex SP-C25	0.5 M NaClO <sub>4</sub>	98 <sup>b</sup>	
	0.1 M Na <sub>2</sub> SO <sub>4</sub>	34 <sup>c</sup>	62 <sup>d</sup>

Same optical spectrum as: <sup>a</sup> a 1:1 mixture of Cr en(H<sub>2</sub>O)<sub>4</sub><sup>3+</sup> and *cis*-Cr en<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup>; <sup>b</sup> 1:2 mixture of Cr en(H<sub>2</sub>O)<sub>4</sub><sup>3+</sup> and *cis*-Cr en<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup>; <sup>c</sup> Cr en(H<sub>2</sub>O)<sub>3</sub><sup>3+</sup> treated similarly with Na<sub>2</sub>SO<sub>4</sub>; <sup>d</sup> *cis*-Cr en<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> treated similarly with Na<sub>2</sub>SO<sub>4</sub>; <sup>e</sup> Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> treated similarly with H<sub>2</sub>SO<sub>4</sub>.

(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>3</sub>.aq and [Cren<sub>3</sub>]<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was obtained. This product was stirred for a few minutes in 1 l of water to remove [Cr en<sub>3</sub>]<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Filtration yielded 25 g of crude [Cr<sub>4</sub>en<sub>6</sub>(OH)<sub>6</sub>](SO<sub>4</sub>)<sub>3</sub>.aq (32 %).

After addition of 100 ml 12 M HCl to the above filtrate, 55 g of [Cr en<sub>3</sub>]Cl<sub>3</sub>.aq containing a little sulfate could be isolated.

4.5 g of finely powdered crude rhodoso sulfate were dissolved in 30 ml ice-cooled 1 M HCl and the solution filtered. 20 g of NaClO<sub>4</sub> were added to the filtrate under stirring and after 30 min the precipitate was filtered off, washed with a little ice-cooled 1 M HClO<sub>4</sub>, then with a 1:1 mixture of 1 M HClO<sub>4</sub> and ethanol, and finally with ethanol and ether. Yield: 4.5 g of [Cr<sub>4</sub>en<sub>6</sub>(OH)<sub>6</sub>](ClO<sub>4</sub>)<sub>6</sub>.-3H<sub>2</sub>O (80 % from the crude sulfate). The product can be reprecipitated almost quantitatively with NaClO<sub>4</sub> from an ice-cooled aqueous solution.

For the cleavage 4.50 g of [Cr<sub>4</sub>en<sub>6</sub>(OH)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub>.-3H<sub>2</sub>O were treated with 5 ml of 12 M HCl for a few min at room temperature, after which the solution, now containing mononuclear complexes, was cooled to 0 °C and saturated with gaseous HCl at this temperature. 5 ml of ice-cooled 70 % HClO<sub>4</sub> were added and the solution was resaturated with gaseous HCl at 0 °C. After 3 days at 5 °C the

precipitate was filtered off, washed with a few drops of ice-cooled 12 M HCl which were afterwards added to the filtrate, then with ice-cooled 4 M HClO<sub>4</sub> and ethanol. Yield: 2.25 g of *cis*-[Cr en<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub> (48 %).

9.5 g of NH<sub>4</sub>Cl were added to the filtrate, and after keeping it overnight at 5 °C the NH<sub>4</sub>ClO<sub>4</sub> was filtered off and 7.7 g of CsCl were added. The filtrate was then resaturated with gaseous HCl at 0 °C and after 6 days at 5 °C the precipitate was filtered off, washed with a 3:1 mixture of methanol and ethanol, and then with ethanol and ether. Yield: 2.1 g of Cs[Cr enCl<sub>4</sub>] (40 %). For purification 6 g of this product were dissolved in 70 ml 12 M HCl; after filtration 10 g of CsCl were added to the filtrate, which was then saturated with gaseous HCl at 0 °C. After a few days at 5 °C 5 g of Cs[Cr enCl<sub>4</sub>] could be isolated as described above.

*Chemicals and apparatus.* All chemicals used were reagent grade or were analysed by us. Cs[Cr enCl<sub>4</sub>] (see above), *cis*-[Cr en<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>) (see above), *cis*-[Cr en<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Br<sub>3</sub>.2H<sub>2</sub>O,<sup>11</sup> *trans*-[Cr en<sub>2</sub>Cl<sub>2</sub>]Cl.H<sub>2</sub>O,<sup>12</sup> *trans*-[Cr en<sub>2</sub>(OH)(H<sub>2</sub>O)]Br<sub>2</sub>.H<sub>2</sub>O,<sup>12</sup> [Cr en<sub>3</sub>]Cl<sub>3</sub>.3H<sub>2</sub>O,<sup>13</sup> *meso*-[en<sub>2</sub>Cr(OH)<sub>2</sub>Cr en<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>,<sup>11</sup> [(OH)en<sub>2</sub>Cr(OH)Cr en<sub>2</sub>(OH)](ClO<sub>4</sub>)<sub>3</sub>.-2H<sub>2</sub>O,<sup>2</sup> [Cr<sub>4</sub>en<sub>6</sub>(OH)<sub>6</sub>](ClO<sub>4</sub>)<sub>6</sub>.3H<sub>2</sub>O/rhodoso (see above), and [Co{(OH)<sub>2</sub>Co en<sub>2</sub>]<sub>3</sub>(NO<sub>3</sub>)<sub>6</sub>.aq<sup>14</sup> were prepared according to, or analogously to, the literature methods and were analysed for Cr(Co), N, and halogen. All analyses agreed within 1–2 % (relative) with the formulae given.

Visible spectra were measured on a Cary 118 spectrophotometer and ESR spectra on a Jeol JES-ME-1X instrument. A Perkin-Elmer 403 apparatus was used for atomic absorption spectrophotometry. The X-ray equipment is referred to in the next section.

*X-Ray diffraction.* X-Ray powder photographs of most of the crystalline compounds were taken using a Guinier camera with CuK $\alpha$  radiation and with silicon as internal standard. Single crystal Weissenberg photographs with CuK $\alpha$  radiation were taken for preliminary purposes, space group determinations *etc.* Some results for salts of b2 and the analogous cobalt(III) compounds are given in Table 5.

*Structure determination of b3 bromide by single crystal X-ray diffraction.* (a) *Crystal data.* Some of the crystal data are given in Table 6. The unit cell dimensions were determined on a Picker FACS-1 diffractometer using MoK $\alpha$  radiation from 24 high-angle reflections by least-squares refinement and were in agreement with those determined from powder photographs. The density of the crystals was determined by flotation in mixtures of 1-bromonaphthalene and 1,2-dibromoethane.

(b) *Data collection.* The diffraction data were collected at 22 °C with a Picker FACS-1 diffrac-

Table 5. X-Ray diffraction data for salts of  $\text{Cr}\{(\text{OH})_2\text{Cr en}_2\}_3^{6+}$  compared with those for the corresponding Werner's brown salts.(a) Guinier powder photographs ( $\text{CuK}\alpha$ )

$[\text{Cr}\{(\text{OH})_2\text{Cren}_2\}_3](\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$				$[\text{Co}\{(\text{OH})_2\text{Coen}_2\}_3](\text{NO}_3)_6 \cdot \text{aq}$		
<i>hkl</i>	Int.	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	Int.	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)
020	w	12.71	12.72	w	12.60	12.57
120	mw	10.60	10.62	w	10.47	10.45
200	w	9.67	9.67	vw	9.40	9.40
$\bar{1}01$	mw	8.49	8.50	w	8.46	8.45
111	mw	8.07	8.06	vw	8.00	8.01
111 }	mw(br.)	7.69	7.67	vw	8.00	8.01
220 }						
021	w	7.42	7.42	w(br.)	7.58	7.53
$\bar{1}21$	vw	7.07	7.06	vw	7.37	7.36
040	vw	6.33	6.36	vw	7.01	7.01
221 }	vw	5.741	5.733	vw	6.28	6.28
320 }						
$\bar{1}41$	mw	5.093	5.090	vw	5.606	5.606
012	m(br.)	4.499	4.499	vw	4.469	4.470
420			4.521	vw	4.398	4.401

Indexing based on:

$a = 19.3_9$  Å  
 $b = 25.4_2$  Å  
 $c = 9.1_6$  Å

$\alpha = \gamma = 90.00^\circ$   
 $\beta = 94.0^\circ$

$a = 18.8_5$  Å  
 $b = 25.1_4$  Å  
 $c = 9.1_1$  Å

$\alpha = \gamma = 90.00^\circ$   
 $\beta = 94.7^\circ$

(b)  $[\text{Co}\{(\text{OH})_2\text{Co en}_2\}_3](\text{S}_2\text{O}_6)_3 \cdot 8\text{H}_2\text{O}$  (Thewalt<sup>27</sup>):Sp.gr.:  $P2_1/n$ 

$a = 9.46_4$  Å,  $b = 22.35_5$  Å,  $c = 22.72_5$  Å,  $\beta = 94.3_3^\circ$

Data from Weissenberg photographs ( $\text{CuK}\alpha$ )

$[\text{Cr}\{(\text{OH})_2\text{Cr en}_2\}_3](\text{S}_2\text{O}_6)_3 \cdot \text{aq}$ : Space group:  $P2_1/n$

$a = 9.5$  Å,  $b = 22.4$  Å,  $c = 23.0$  Å,  $\beta = 94.6^\circ$

tometer from a single crystal,  $0.19 \times 0.10 \times 0.27$  mm<sup>3</sup> in the  $a$ -,  $b$ -, and  $c$ -direction, respectively, using graphite monochromated  $\text{MoK}\alpha$  radiation. A  $\theta - 2\theta$  scan mode was used with a rate in  $2\theta$  of  $1^\circ \text{ min}^{-1}$ . The scan range was from  $2\theta_0 - (1.5^\circ + 0.346^\circ \tan \theta)$  to  $2\theta_0 + (1.7^\circ + 0.346^\circ \tan \theta)$ . Background counts were made for 20 s at each end of the scan range. The intensities of five standard reflections were measured after each 40 reflections and these measurements showed that no deterioration or misalignment of the crystal occurred during the data collections.

Intensity data were collected for two symmetry-related sets of reflections,  $5.5^\circ < 2\theta \leq 54^\circ$ :

Set 1: octants  $hkl$  and  $h\bar{k}\bar{l}$ .Set 2: octants  $hkl$  and  $h\bar{k}l$ .

The graphite crystal in the monochromator had to be renewed between the measurements of set 1 and set 2.

The two sets were corrected for Lorentz and polarization effects, and a Gaussian numerical integration procedure<sup>15</sup> was used for absorption correction (grid:  $8 \times 6 \times 6$  sampling points; the transmission factors varied between 0.39 and 0.56). The two sets were then averaged after the application of a scale factor to one of the sets. The  $R_s$  value between symmetry related reflections were 0.056 ( $R_s = \sum_{hkl} \sum_i |F_s|^2 - |F_i|^2| / \sum_{hkl} \sum_i |F_i|^2$ , where  $F_s$  designates the averaged structure amplitude and  $F_i$  the amplitudes for the individual measurements). This resulted in 4469 independent reflections which were reduced to 3319 observed reflections using the

Table 6. Crystal data for  $[\text{en}_2\text{Cr}(\text{OH})_2\text{Cr en}(\text{OH})_2\text{-Cr en}(\text{OH})_2\text{Cr en}_2]\text{Br}_6 \cdot 2\text{H}_2\text{O}$ .

Molecular weight for  $\text{Cr}_4\text{C}_{12}\text{H}_{58}\text{N}_{12}\text{O}_8\text{Br}_6$ : 1186.1

Monoclinic:  $a = 15.470(4) \text{ \AA}$ ,  $b = 16.420(4) \text{ \AA}$ ,  
 $c = 7.952(3) \text{ \AA}$ ,  $\beta = 99.364(18)^\circ$ ;  
 $V = 1993.0 \text{ \AA}^3$ .

Density:  $d_{\text{obs}} = 2.00_3 \text{ g/cm}^3$ ,  $d_{\text{calc}} = 1.976 \text{ g/cm}^3$   
 for  $Z = 2$ .

$\mu(\text{MoK}\alpha) = 70.6 \text{ cm}^{-1}$ ,  $F(000) = 1168$ .

Systematically absent reflections:  $h0l$ :  $h + l \neq 2n$   
 $0k0$ :  $k \neq 2n$

Space group:  $P2_1/n$

General equivalent positions:  $x, y, z$   $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$   
 $x, \bar{y}, \bar{z}$   $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

Developed faces:  $\{110\}$ ,  $\{011\}$ , and  $\{010\}$

criterion  $I > 2\sigma(I)$ , where  $\sigma(I)$  is the standard deviation calculated by counting statistics.

The following programs were used for computation: The Vanderbilt System<sup>16</sup> for diffractometer operations, an absorption correction program and a data reduction program both of local origin, ORTEP II for the illustrations,<sup>17</sup> the X-Ray

System<sup>18</sup> for the crystal structure analysis, and Simplex<sup>19</sup> for the weighting analysis.

The atomic scattering factors used were those reported by Cromer and Mann<sup>20</sup> for the uncharged atoms; for hydrogen the factor calculated by Stewart *et al.*<sup>21</sup> was used. The anomalous dispersion corrections for chromium and bromine were taken from Cromer and Liberman.<sup>22</sup>

(c) *Structure determination and refinement.* The three-dimensional Patterson function calculated from 2300 independent reflections from the first data set showed the octahedral ligand arrangement around the chromium atoms, and a Fourier synthesis based on a centrosymmetric tetranuclear chromium skeleton including oxygen and nitrogen ligands revealed the positions of the bromine atoms. Another approach to the solution was a Harker section analysis of the Patterson function, which revealed the positions of the bromine and chromium atoms, and Fourier syntheses based on these gave the positions of the nitrogen and oxygen ligand atoms, which, when included, showed the positions of the carbon atoms and one oxygen from water of crystallization (O4).

The final analysis was based on the 3319 independent reflections considered observed from the two data sets. Hamilton *R*-ratio tests were used as an aid to select the simplest model compatible with the data. Full-matrix least-squares refinement minimiz-

Table 7. b3 Bromide. Final fractional coordinates with e.s.d. The labelling is explained in Fig. 7. Parameters for hydrogen atoms are given in Table 9.

Atom	x	y	z
Br 1	0.17945(6)	0.11369(5)	0.00796(8)
Br 2	0.79243(4)	0.20916(4)	0.11472(9)
Br 3	0.47245(5)	0.13791(5)	0.35077(12)
Cr 1	0.26100(5)	-0.01301(5)	0.56393(10)
Cr 2	0.07722(5)	0.05486(5)	0.48991(10)
O 1	0.1839(2)	0.0472(3)	0.3908(6)
O 2	0.1579(2)	-0.0004(2)	0.6745(5)
O 3	-0.0277(3)	0.0499(3)	0.5976(6)
O 4	0.4300(4)	0.3432(5)	0.3551(9)
N 1	0.2165(3)	-0.1266(3)	0.4740(6)
N 2	0.3530(3)	-0.0350(3)	0.4048(7)
N 3	0.3380(3)	-0.0663(3)	0.7730(6)
N 4	0.3266(3)	0.0902(3)	0.6710(7)
N 5	0.1029(4)	0.1723(3)	0.5851(7)
N 6	0.0105(3)	0.1190(3)	0.2830(6)
C 1	0.2793(4)	-0.1652(4)	0.3767(8)
C 2	0.3179(5)	-0.0986(4)	0.2798(8)
C 3	0.3758(4)	-0.0034(4)	0.8969(8)
C 4	0.4035(4)	0.0680(4)	0.7992(9)
C 5	0.0403(4)	0.2297(4)	0.4855(8)
C 6	0.0324(5)	0.2067(4)	0.3002(8)



Table 8. b3 Bromide. Final thermal parameters,  $u_{ij} \times 100(\text{\AA}^2)$ , with e.s.d. The expression for the temperature factors is  $\exp\{-2\pi^2(u_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2u_{12}hka^*b^* + 2u_{13}hla^*c^* + 2u_{23}klb^*c^*)\}$ . Parameters for hydrogen atoms are given in Table 9.

Atom	$u_{11}$	$u_{22}$	$u_{33}$	$u_{12}$	$u_{13}$	$u_{23}$
Br 1	9.36(6)	6.61(5)	2.92(3)	1.79(4)	1.47(3)	-0.15(3)
Br 2	4.07(3)	2.95(3)	5.29(3)	-0.06(2)	1.47(3)	0.48(3)
Br 3	3.77(3)	5.50(4)	8.88(6)	0.71(3)	2.27(4)	1.75(4)
Cr 1	1.91(4)	2.17(4)	2.68(4)	0.06(3)	0.27(3)	0.35(3)
Cr 2	1.74(4)	2.06(4)	2.23(4)	-0.04(3)	0.13(3)	0.14(3)
O 1	2.55(19)	4.0(2)	2.8(2)	0.32(16)	0.74(17)	1.11(19)
O 2	2.48(18)	2.9(2)	2.7(2)	0.16(15)	0.24(15)	0.26(17)
O 3	2.8(2)	3.1(2)	2.6(2)	-0.20(16)	0.48(17)	-0.89(19)
O 4	7.8(4)	12.6(6)	9.1(5)	0.3(4)	2.5(4)	5.4(5)
N 1	3.1(3)	3.4(3)	3.5(3)	-0.4(2)	0.8(2)	0.2(2)
N 2	3.4(3)	3.8(3)	5.0(3)	0.4(2)	1.4(2)	0.9(2)
N 3	2.5(2)	3.4(3)	3.8(3)	0.17(19)	0.50(19)	0.8(2)
N 4	3.8(3)	3.0(3)	5.3(3)	-0.5(2)	-0.7(2)	0.6(2)
N 5	3.2(3)	2.9(2)	3.3(3)	-0.5(2)	0.0(2)	0.1(2)
N 6	2.5(2)	3.3(3)	3.1(3)	0.5(2)	0.1(2)	0.2(2)
C 1	5.3(4)	3.6(3)	4.2(3)	0.7(3)	1.1(3)	-0.7(3)
C 2	5.5(4)	4.7(4)	4.1(3)	0.6(3)	1.9(3)	-0.2(3)
C 3	3.6(3)	5.2(4)	3.2(3)	-0.4(3)	-0.6(2)	-0.1(3)
C 4	3.3(3)	4.0(3)	5.5(4)	-0.5(3)	-1.1(3)	0.2(3)
C 5	4.0(3)	3.2(3)	4.4(4)	0.9(3)	0.0(3)	-0.4(3)
C 6	4.5(4)	3.5(3)	3.8(3)	0.2(3)	0.3(3)	1.1(3)

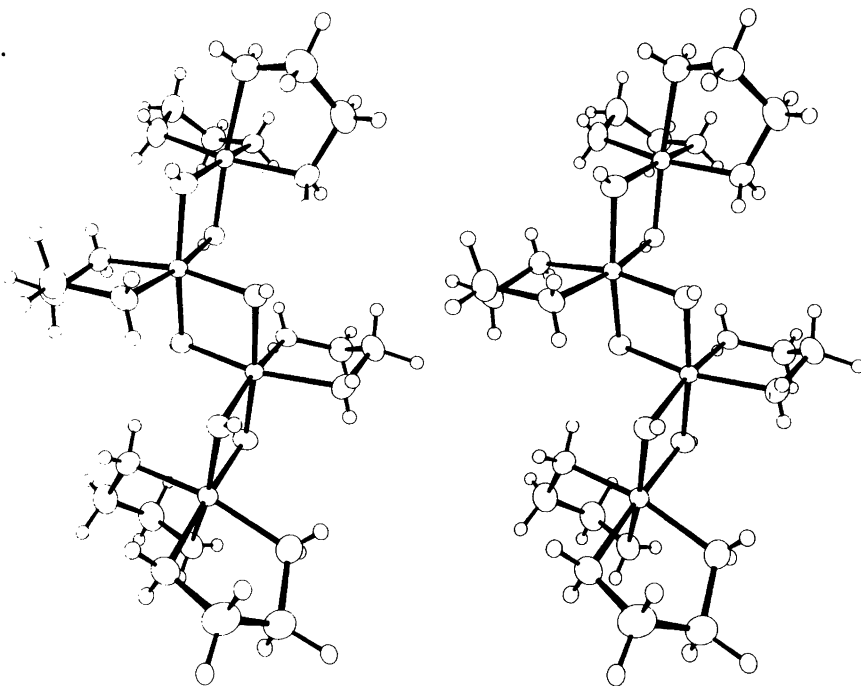


Fig. 5. Stereoscopic drawing of the b3 complex ion. The thermal ellipsoids enclose 50 % probability with the exception of hydrogen atoms, which are shown as spheres with 0.1 Å radius. The four chromium atoms in the molecule are surrounded octahedrally by ethylenediamine and di- $\mu$ -hydroxo groups.

Table 9. b3 Bromide. Final hydrogen atom parameters with e.s.d. The labelling is explained in Fig. 7. The temperature factors are  $\exp(-8\pi^2 U \sin^2 \theta/\lambda)$ .

Atom	x	y	z	$U \times 100(\text{\AA}^2)$
H 1	0.185(5)	0.061(5)	0.317(9)	4(3)
H 2	0.155(6)	0.015(5)	0.754(11)	7(3)
H 3	-0.027(4)	0.060(4)	0.665(8)	2(2)
H 4	0.160(4)	-0.119(4)	0.417(8)	3.5(17)
H 5	0.205(4)	-0.154(4)	0.546(7)	3.1(15)
H 6	0.324(3)	-0.192(3)	0.458(6)	1.7(12)
H 7	0.254(4)	-0.200(4)	0.297(8)	4.5(18)
H 8	0.363(5)	-0.120(5)	0.239(10)	8(3)
H 9	0.266(4)	-0.073(4)	0.185(8)	5.0(19)
H 10	0.396(3)	-0.052(3)	0.459(6)	2.0(13)
H 11	0.360(4)	0.006(4)	0.349(8)	4.2(17)
H 12	0.375(4)	-0.090(3)	0.740(7)	2.7(15)
H 13	0.307(5)	-0.104(5)	0.810(9)	6(2)
H 14	0.332(5)	0.016(5)	0.959(9)	6(2)
H 15	0.421(5)	-0.022(4)	0.968(9)	5(2)
H 16	0.425(6)	0.117(5)	0.873(11)	8(3)
H 17	0.446(5)	0.055(5)	0.736(10)	8(3)
H 18	0.297(7)	0.125(6)	0.728(14)	12(4)
H 19	0.338(4)	0.109(4)	0.611(7)	2.9(16)
H 20	0.147(4)	0.183(4)	0.571(7)	1.7(15)
H 21	0.097(5)	0.169(4)	0.689(10)	5(2)
H 22	-0.017(6)	0.229(5)	0.517(11)	7(3)
H 23	0.064(5)	0.291(5)	0.508(9)	6(2)
H 24	-0.003(6)	0.233(5)	0.231(11)	8(3)
H 25	0.091(4)	0.223(4)	0.272(8)	3.4(16)
H 26	-0.042(4)	0.108(3)	0.271(7)	2.1(14)
H 27	0.023(5)	0.105(4)	0.186(9)	5(2)

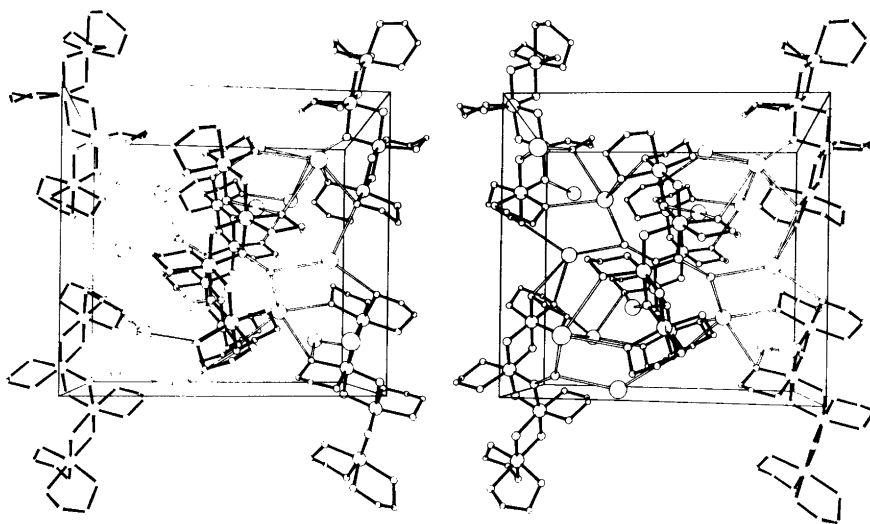


Fig. 6. Stereoscopic drawing of the unit cell content of b3 bromide. The radii of the spheres symbolizing Br, Cr, O, N, and C are 0.30, 0.25, 0.15, 0.125, and 0.10 Å, respectively. The view is along the negative  $c$ -axis, having the  $a$ -axis going down and the  $b$ -axis right.

Table 10. b3 Bromide. Bond lengths and contact distances (Å) with e.s.d.

Cr 1—O 1	1.939(4)	N 1—C 1	1.480(9)
Cr 1—O 2	1.954(4)	N 2—C 2	1.483(8)
Cr 2—O 1	1.945(4)	N 3—C 3	1.480(8)
Cr 2—O 2	1.984(4)	N 4—C 4	1.480(8)
Cr 2—O 3	1.956(5)	N 5—C 5	1.485(8)
Cr 2—O 3'	1.964(4)	N 6—C 6	1.480(8)
Cr 1—N 1	2.075(5)	C 1—C 2	1.515(10)
Cr 1—N 2	2.084(6)	C 3—C 4	1.506(10)
Cr 1—N 3	2.074(5)	C 5—C 6	1.507(9)
Cr 1—N 4	2.084(5)		
Cr 2—N 5	2.086(5)	O 1—H 1	0.63(7)
Cr 2—N 6	2.081(5)	O 2—H 2	0.69(9)
		O 3—H 3	0.56(6)

N—H: 0.7–0.9; average 0.81(7)

C—H: 0.9–1.1; average 0.96(7)

O3(in(.9723, .0499, .5976))—O4(in(.9300, .1568, .8551)): 2.853(9)

Contact distances Br—O and Br—N: 3.2–3.5

ing  $R = \sum w(|F_o| - K|F_c|)^2$  with the positional parameters and anisotropic temperature factors of the 3 Br, 2 Cr, 4 O, 6 N, and 6 C atoms led to an  $R$ -value of 0.052. A difference Fourier analysis showed the positions of all hydrogen atoms except those in the water molecule, and further refinement with two blocks including positions and isotropic temperature factors of hydrogen atoms and with application of a weighting scheme,  $1/w = 3.59 + 2.11\sigma^2(F) + 0.036|F| + 0.00029|F|^2 - 5.75 \sin \theta/\lambda$  (the coefficients were obtained as described by

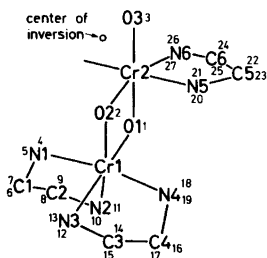


Fig. 7. Labelling of the atoms in the b3 complex molecule. Small numbers symbolize hydrogen atoms. The atoms in the other half of the molecule, symmetrically connected through the centre of inversion, are in Tables 10 and 11 labelled with primes: Cr2', O3' etc.

Nielsen<sup>19</sup>), gave a final  $R$ -value of 0.044 and  $R_w = 0.048$  (average shift/error 0.03, max. 0.3). The final results of this structure analysis are given in Tables 6–11 and Figs. 5–7. A list of observed and calculated structure amplitudes is available from the authors upon request.

## RESULTS AND DISCUSSION

The polynuclear complexes involved in this investigation are, in order of increasing charge (see Table 1):

$en_2Cr(OH)_2Cr en_2^{4+}$ . This di- $\mu$ -hydroxo-bis[bis(ethylenediamine)chromium(III)] ion, often called the diol, exists in racemic  $(\Delta\Delta/\Lambda\Lambda)^3$  and *meso*  $(\Delta\Lambda)^2$  forms, and the latter has been established by X-ray diffraction.<sup>23,24</sup> The *meso*-form was identified as a major part of the first polynuclear chromatographic band from separations of Cr(II)+charcoal catalyzed equilibrium solutions with  $C_{Cr} \approx 0.01$  M.<sup>8</sup> In basic solution the cation of the *meso*-form is eluted at almost the same rate as  $Cr en_3^{3+}$ , but in acidic solution somewhat slower. It was isolated as the iodide and identified by means of X-ray powder diffraction and ESR. The *meso*-diol perchlorate<sup>11</sup> was used as a model compound to follow the hydrolysis with 70% perchloric acid using ESR spectroscopy. Fig. 4 shows that the hydrolysis product after 10–15 h at room temperature is pure *cis*- $Cr en_2(H_2O)_2^{3+}$ , and that the reaction proceeds via a species with an ESR spectrum similar to that of  $[(OH)en_2Cr(OH)Cr en_2(OH)](ClO_4)_3 \cdot 2H_2O$  in 4 M  $HClO_4$ , presumably  $(H_2O)en_2Cr(OH)Cr en_2(H_2O)^{5+}$ .<sup>2</sup> We found hydrolysis at room temperature (at the end increased to 70 °C) with 1 M  $HClO_4$  to be much slower than with 12 M  $HClO_4$ , and ESR spectra showed that the products are a mixture of polynuclear species, *cis*- $Cr en_2(H_2O)_2^{3+}$ , and apparently mononuclear species with less than four nitrogen coordinated per chromium atom (*cf.* Mønsted's investigation of the acid hydrolysis of chromium(III) amines<sup>25</sup>).

$en_2Cr(OH)_2Cr en(OH)_2Cr en_2^{5+}$ . This  $\mu$ -{mono(ethylenediamine)bis(dihydroxo)chromium(III)}-bis[bis(ethylenediamine)chromium(III)] ion, a, constitutes a major part of the a-band from the chromatographic separation. This new complex has so far only been isolated in satisfactorily crystalline form as the nitrate. The identification was based on chemical analysis (Table 2) and on analysis of the products obtained on hydrolysis in 70% perchloric acid; the two methods applied both showed the

Table 11. b3 Bromide. Selected bond angles (°) with e.s.d.

O 1—Cr 1—O 2	79.2(2)	Cr 1—O 1—Cr 2	102.1(2)
O 1—Cr 2—O 2	78.3(2)	Cr 1—O 2—Cr 2	100.2(2)
O 3—Cr 2—O 3'	79.3(2)	Cr 2—O 3—Cr 2'	100.7(2)
N 1—Cr 1—N 2	81.7(2)	Cr 1—N 1—C 1	110.8(4)
N 3—Cr 1—N 4	80.7(2)	Cr 1—N 2—C 2	108.5(4)
N 5—Cr 2—N 6	81.9(2)	Cr 1—N 3—C 3	110.6(4)
		Cr 1—N 4—C 4	111.4(4)
O 1—Cr 2—O 3'	96.2(2)	Cr 2—N 5—C 5	108.9(4)
O 2—Cr 2—O 3	97.1(2)	Cr 2—N 6—C 6	110.0(4)
O 2—Cr 2—O 3'	91.4(2)		
O 1—Cr 1—N 1	94.7(2)	N 1—C 1—C 2	107.7(5)
O 1—Cr 1—N 2	93.4(2)	N 2—C 2—C 1	107.4(5)
O 1—Cr 1—N 4	94.5(2)	N 3—C 3—C 4	108.3(5)
O 2—Cr 1—N 1	90.1(2)	N 4—C 4—C 3	106.4(5)
O 2—Cr 1—N 3	95.1(2)	N 5—C 5—C 6	107.7(5)
O 2—Cr 1—N 4	96.2(2)	N 6—C 6—C 5	108.4(5)
O 1—Cr 2—N 5	94.8(2)		
O 1—Cr 2—N 6	93.3(2)	Other tetrahedral angles	
O 2—Cr 2—N 5	95.4(2)	involving H: ~102–117(5)	
O 3—Cr 2—N 5	90.1(2)	H 1—O 1—Cr 1	137(7)
O 3—Cr 2—N 6	91.6(2)	H 1—O 1—Cr 2	120(7)
O 3'—Cr 2—N 6	92.8(2)	H 2—O 2—Cr 1	129(7)
		H 2—O 2—Cr 2	112(7)
N 1—Cr 1—N 3	90.7(2)	H 3—O 3—Cr 2	121(7)
N 2—Cr 1—N 3	93.1(2)	H 3—O 3—Cr 2'	122(7)
N 2—Cr 1—N 4	93.1(2)		
Dihedral angles:	N 1—C 1—C 2—N 2	53.4(6)	
	N 3—C 3—C 4—N 4	51.9(6)	
	N 5—C 5—C 6—N 6	52.9(7)	

latter products to be *cis*-Cr en<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> and Cr en(H<sub>2</sub>O)<sub>4</sub><sup>3+</sup> in 2:1 ratio (see Tables 3 and 4).

$\text{en}_2\text{Cr} \begin{array}{l} \text{OH} - \text{Cr en} - \text{OH} \\ \text{(OH)}_2 \\ \text{OH} - \text{Cr en} - \text{OH} \end{array} \text{Cr en}_2^{6+}$ . This  $\mu$ -{di- $\mu$ -hydroxo-bis[mono(ethylenediamine)*trans*-dihydroxochromium(III)]}-bis[bis(ethylenediamine)-chromium(III)] ion, the rhodoso, was first isolated by Pfeiffer<sup>1</sup> and later shown by X-ray diffraction to have the indicated structure in the *meso*-form.<sup>4</sup> It is eluted at the same rate as the b-band but was not found in this band. In this work rhodoso served as a model compound for the hydrolysis in 70% perchloric acid and is in this medium hydrolyzed to give *cis*-Cr en<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> and Cr en(H<sub>2</sub>O)<sub>4</sub><sup>3+</sup> in 1:1 ratio (see Tables 3 and 4, and Fig. 2). After hydrolysis with 12 M hydrochloric acid 48% of the chromium was isolated as *cis*-[Cr en<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>) and 40% as Cs[Cr enCl<sub>4</sub>] (see experimental section).

$\text{Cr}\{(\text{OH})_2\text{Cr en}_2\}_3^{6+}$ . This tris[di- $\mu$ -hydroxo-bis(ethylenediamine)chromium(III)]chromium(III) ion was the first new polynuclear complex to be isolated from the Cr(II)+charcoal catalyzed equilibrium solutions,<sup>8,26</sup> and constitutes a major part, b2, of the b-band from the chromatographic separations. It is the chromium analogue of the cobalt(III) complex often referred to as Werner's brown salt.<sup>14</sup> The structure of the dithionate of the cobalt species has been established by X-ray diffraction,<sup>27</sup> and comparison of Weissenberg films of this compound (kindly placed at our disposal by U. Thewalt) with those of the chromium dithionate unambiguously demonstrated the isomorphism. The chromium dithionate was prepared nearly quantitatively by metathesis from the nitrate, and one may assume the configurations around the four chromium atoms to be  $\Delta\{\Delta\Delta\Delta\}/\Delta\{\Lambda\Delta\Delta\}$  as in the cobalt dithionate. X-Ray powder photographs of the nitrates of the

cobalt and chromium complexes likewise showed isomorphism. Some of the X-ray data are given in Table 5.

Analysis of the products of hydrolysis of the b2 nitrate with 70% perchloric acid showed them to consist of  $cis-Cr en_2(H_2O)_2^{3+}$  and  $Cr(H_2O)_6^{3+}$  in 3:1 ratio (Fig. 2 and Tables 3 and 4).

$\Delta\Delta\Delta\Delta-en_2Cr(OH)_2Cr en(OH)_2Cr en(OH)_2Cr en_2^{6+}$ . This  $\mu$ -{di- $\mu$ -hydroxo-bis[mono(ethylenediamine)*cis*-dihydroxochromium(III)]}-bis[bis(ethylenediamine)chromium(III)] ion was found as a minor constituent, b3, in the b-band. This new complex readily forms nice crystals of, e.g., the bromide and the nitrate. Hydrolysis of the nitrate with 70% perchloric acid gave  $cis-Cr en_2(H_2O)_2^{3+}$  and  $Cr en(H_2O)_4^{3+}$  in 1:1 ratio (Fig. 2 and Tables 3 and 4).

The X-ray structure analysis (see the experimental section) of the bromide showed that the complex ions all lie on centres of inversion, that the configuration of this centrosymmetric *meso* form is  $\Delta\Delta\Delta\Delta$ , and that the ring conformations are  $lel_e$ , i.e. all the C-C bonds are parallel to the pseudo threefold axis of the metal atoms. Bond distances and angles in the complex are in excellent agreement with those found for similar structures, cf., e.g., that of *meso*-[ $en_2Cr(OH)_2Cr en_2$ ]( $ClO_4$ ) $_2Cl_2 \cdot 2H_2O$ .<sup>23</sup>

$Cr_4en_6(OH)_6^{6+}$ . This b1 compound was isolated in low yield from the b-band as a crystalline red-violet nitrate. Hydrolysis of this nitrate with 70%

perchloric acid produced  $cis-Cr en_2(H_2O)_2^{3+}$  and  $Cr en(H_2O)_4^{3+}$  in 1:1 ratio. The formula  $Cr_4en_6(OH)_6^{6+}$  embraces all the 6+-charged complexes mentioned above, but the b1 nitrate differs in many respects from the others, e.g. in solubility and optical spectrum (which is very closely similar to that of the a nitrate, see Fig. 8), and no isomorphism could be demonstrated by X-ray powder diffraction. We intend to try to grow larger crystals for single crystal X-ray analysis.

The above argument for ascribing the structure  $en_2Cr(OH)_2Cr en(OH)_2Cr en_2^{5+}$  to a rested, apart from elemental microanalysis, solely on analysis of the hydrolysis products. However, in the better established cases (diol, rhodoso, b2, and b3) this hydrolysis produced the mononuclear aquaamines with full retention of configuration. It is also noteworthy that only one charge type has been found so far within each band from the ion-exchange separations on Sephadex SP-C25, the rate of elution decreasing with increasing charge. The assignment of a charge of 5+ to a is then consistent with this "rule". Furthermore it is characteristic that apart from the diol all of these polynuclear complexes exhibited very small changes in their visible spectra on going from acidic to basic medium (<1–2 nm for the first spin-allowed absorption band). This is as would be expected for chromium(III) amine complexes lacking  $H_2O$  or terminal  $OH^-$  ligands. The ESR spectra showed the same pH-independency ( $3 < pH < 9$ ), with the exception

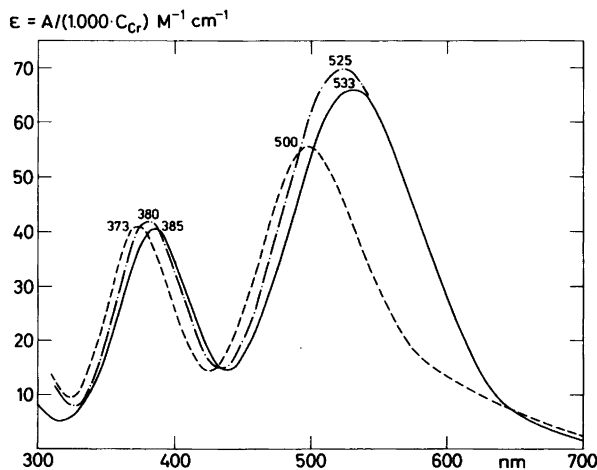


Fig. 8. Optical spectra of: a nitrate (---), b2 nitrate (----), and b3 bromide (—) in water. The spectra showed no changes after 5–10 min.

of that for the diol, which under these conditions (aqueous solutions at room temperature) undergoes opening of one of the OH-bridges<sup>2</sup> (see later).

This same sort of argumentation leads to the formula for b1, namely  $\text{Cr}_4\text{en}_6(\text{OH})_6^{6+}$ , consisting of 2 *cis*-Cr en<sub>2</sub>- and 2 Cr en-moieties connected by OH-bridges.

It seems to be characteristic that most of the above-mentioned complexes remain unchanged for hours in acidic (concentrated mineral acids excepted) and neutral solution. However, as mentioned above, the diol opens one of the OH-bridges,<sup>2,3</sup> but similar phenomena have yet to be examined further for the other complexes containing di- $\mu$ -hydroxo groups.

Chromium(III) in these amine buffers seems to prefer condensation *via* di- $\mu$ -hydroxo bridge formation. Fig. 9 shows the 4+ - to 6+ - charged skeletons of such edge-sharing octahedra with the free edges imagined occupied by chelating ethylenediamine. Except for II and III they all have the chromium atoms in the same plane. The number of configurational isomers is of course much higher than the number of skeletons, and if one includes the different combinations of ring conformations the number of isomers is enormous (208 for the brown salt<sup>28</sup>). In Fig. 9 the configurational  $\Delta$  and  $\Lambda$  designations are quoted where determined by the

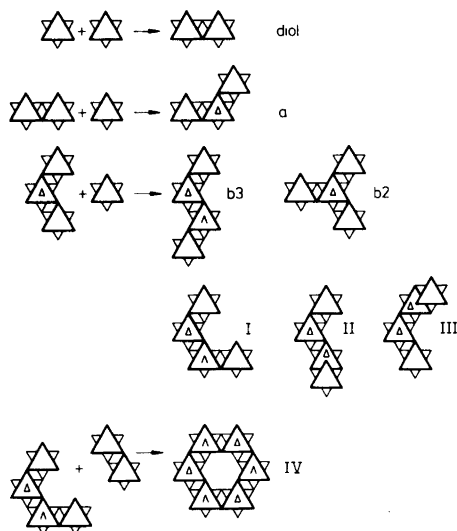
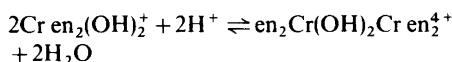


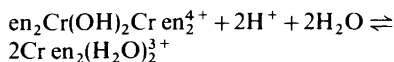
Fig. 9. The 4+ - to 6+ - charged skeletons of edge-sharing octahedra with the free edges occupied by chelating ethylenediamine.

di- $\mu$ -hydroxo groups. The chromium atoms without this designation may have either  $\Delta$  or  $\Lambda$  configuration. Thus the skeleton b3 gives two *meso*-forms, namely the  $\Delta\Lambda\Delta\Lambda$  found in the b3 bromide and a  $\Lambda\Lambda\Delta\Delta$ -form, both with a centre of inversion. Likewise the skeleton I has two *meso*-forms,  $\Delta\Lambda\Delta\Lambda$  and  $\Lambda\Lambda\Delta\Delta$ , both with a symmetry plane. In addition b3 as well as I have a racemic form,  $\Delta\Lambda\Delta\Delta/\Lambda\Delta\Delta\Lambda$ .

After having established equilibrium among the mononuclear species in the chromium(III) ethylenediamine system we observed<sup>8</sup> that, when the catalyst was removed, the solutions had a tendency to form more of the polynuclear species at the expense of the mononuclear ones during the next months. This phenomenon was more pronounced at lower pH, and was observed even more markedly in similar investigations in ammonia buffers.<sup>9</sup> The concentration ratios for the various mononuclear complexes were, however, maintained. Thus, whereas equilibrium involving only mononuclear chromium(III) amines could be demonstrated, this was not so for reactions involving polynuclear complexes. Chromium(III) ethylenediamine buffers kept at 40–50 °C for 3–5 days did not differ much in composition from the chromium(II) + charcoal catalyzed ones (room temperature), and likewise we observed the same final distribution of species when starting with another chromium(III) compound than  $\text{Cr en}_3^{3+}$  (rhodoso was tried). A common feature was that the amount of polynuclear species increased with increasing chromium concentration and decreasing pH in the investigated pH interval. This is in accordance with what would be expected from pure equilibrium considerations for the formation of polynuclear amine complexes containing oxygen solely in the form of OH-bridges, *e.g.*



In still more acidic media mononuclear species should again be favoured:



The present difficulties in isolating the polynuclear complexes quantitatively make it impossible to tell exactly how much of the involved species are present in the ethylenediamine system. There is no doubt that other isomers are there, some of which are suggested in connection with Fig. 9. On the

other hand, most of the chromium species with charges up to +6 have been accounted for, and there is little doubt that the fractions which are eluted more slowly on Sephadex SP-C 25 than the b-band contain polynuclear complexes of higher charge and with more than four chromium atoms per molecule. Some of them will probably prove to belong to the many isomers obtained by adding an extra di- $\mu$ -hydroxo bridged chromium to the tetranuclear complexes shown in Fig. 9.

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