Synthesis and Properties of μ-Carboxylato-O,O-μ-hydroxobis-[bis(ethylenediamine)chromium(III)] Salts with Acetate, Formate and Glycinate as Bridging Groups

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

Reaction of *meso* diol, Δ,Λ-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$]$^{4+}$, with carboxylic acids gives carboxylato-O,O bridged complexes of the type Δ,Λ-[(en)$_2$Cr(RCOO)(OH)Cr(en)$_2$]$^{4+}$ and crystalline salts have been isolated for R=CH$_3$−, H−, $^+$H$_3$NCH$_2$− and H$_2$NCH$_2$−. Salts of the racemic compounds, Δ,Δ- and Λ,Λ-[(en)$_2$Cr(RCOO)(OH)Cr(en)$_2$]$^{4+}$, were synthesized by similar methods.

The proposed structures, with the two carboxylate oxygens each coordinated symmetrically to a chromium(III) atom, are unambiguously based upon the infrared spectra, visible absorption spectra and protolytic properties of the complexes. The formation of these carboxylato bridged complexes is relatively fast and pseudo first-order rate constants in 4 M RCOOH determined spectrophotometrically were all in the region $(1-7)\times 10^{-4}$ s^{-1} (25 °C).

These complexes are robust in acid solution but hydrolyze fairly rapidly in basic solution. In strong base the initial process is deprotonation of the hydroxo bridge (p$K_a \simeq 12$), giving blue μ-carboxylato-μ-oxo complexes. The acid dissociation constants, K_a, of the ammonium group in the glycinato complexes were determined by glass electrode measurements (pK_a=7.5 for both isomers, 1 M NaClO$_4$, 20 °C).

A linear correlation between the antisymmetric stretching frequencies ν_{as}(CO) of the carboxylato bridge and pK_a for the corresponding carboxylic acid made it possible to estimate pK_a for H$_2$NCH$_2$-COOH (pK_a=4.3, I=0, 25 °C).

Several binuclear cobalt(III) complexes with carboxylate bridging groups have been described in literature and among the most studied complexes are [(NH$_3$)$_4$Co(RCOO)(NH$_2$)Co(NH$_3$)$_4$]$^{4+}$ and [(NH$_3$)$_3$Co(RCOO)(OH)$_2$Co(NH$_3$)$_3$]$^{3+}$, which are easily obtained from the corresponding amidohydroxo and trihydroxo bridged complexes.[1−4] In all these complexes the carboxylate forms a symmetrical bridge in which both of the carboxylate oxygens are bound to the cobalt(III) centres.

Studies on well-characterized aniono chromium(III) binuclear complexes are few, and carboxylate bridged complexes have never been isolated.[5−7] Recently it was shown that the *meso* (Δ,Λ) and the *racemic* (Δ,Δ- and Λ,Λ) ethylenediamine diols, [(en)$_2$Cr(OH)$_2$Cr(en)$_2$]$^{4+}$, rapidly attain equilibrium with their corresponding monools, [(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$(OH)]$^{4+}$, which have been isolated as salts.[8,9] For both isomers cleavage of the hydroxo bridge of the monools occurs orders of magnitude slower than the hydroxo bridge cleavage of the diols. These results clearly suggested the prospects of substitution reactions in analogy with the cobalt(III) chemistry mentioned above, and it was recently shown that *meso* diol reacts rapidly and quantitatively with sulfuric acid giving a sulfato bridged complex, Δ,Λ-[(en)$_2$Cr(OH)(SO$_4$)Cr(en)$_2$]$^{3+}$.[5]

In this work, reactions of the ethylenediamine diols with carboxylic acids have been studied and

novel carboxylato bridged complexes are characterized. The results are of relevance to the chemistry involved in chromium(III) tanning processes, where the formation of carboxylato bridged polynuclear complexes is often postulated.[10−13]

The following ligand abbreviations have been used, ac = acetate, form = formate, gly = glycinate = aminoacetate = $H_2NCH_2COO^-$, glyH = ammonioacetate = $^+H_3NCH_2COO^-$, en = ethylenediamine = 1,2-diaminoethane.

RESULTS AND DISCUSSION

Preparations. Carboxylato-*O,O* bridged complexes of acetic acid, formic acid and glycine were prepared from their parent monools or diols by reaction with a large excess of the carboxylic acid. In the following the syntheses of the individual compounds are briefly commented on.

When *meso* diol perchlorate, Δ,Λ-[(en)$_2$Cr(OH)$_2$-Cr(en)$_2$](ClO$_4$)$_4$, was dissolved in 4 M acetic acid at room temperature, the colour of the solution changed within some hours from reddish-purple to red due to the formation of a μ-acetato-μ-hydroxo complex. The complex was isolated as the tetrachlorozincate, Δ,Λ-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$]-(ZnCl$_4$)$_2$.H$_2$O. The tetrachlorozincate was readily and in high yield converted to the perchlorate dihydrate. Similarly, reaction of *meso* diol perchlorate in 2 M formic acid gave a μ-formato-μ-hydroxo complex isolated as the tetrachlorozincate, Δ,Λ-[(en)$_2$Cr(form)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$. This salt was readily converted to the perchlorate. The glycine carboxylato-*O,O* bridged complex was made by reacting *meso* diol chloride with 2 M glycinium chloride in 0.5 M hydrochloric acid at 55 °C. At this temperature the reaction is rapid ($t_{\frac{1}{2}} \leq 10$ min) and Δ,Λ-[(en)$_2$Cr(glyH)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$.Cl.-4H$_2$O could be isolated. In this salt the non-ligating amino group in glycine is protonated. From this protonated form the corresponding deprotonated complex was, after removal of zinc as Zn(OH)$_2$, isolated as the red bromide, Δ,Λ-[(en)$_2$Cr(gly)(OH)-Cr(en)$_2$]Br$_4$.4H$_2$O.

The *racemic* carboxylato-*O,O* bridged complexes were synthesized by methods similar to those described above for the *meso* complexes. Some modifications have been made and these are essentially dictated by difference in solubilities. Generally the *racemic* salts are much more soluble than the corresponding *meso* salts. Furthermore,

racemic monool, Δ,Δ- and Λ,Λ-[(H$_2$O)(en)$_2$Cr(OH)-Cr(en)$_2$(OH)]Br$_4$.H$_2$O, is more readily available than its corresponding diol and subsequently monool was used in all preparations of *racemic* complexes.

The *racemic* acetato and formato bridged complexes were both isolated as tetrachlorozincates, Δ,Δ- and Λ,Λ-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$.-H$_2$O and Δ,Δ- and Λ,Λ-[(en)$_2$Cr(form)(OH)Cr(en)$_2$]-(ZnCl$_4$)$_2$. The tetrachlorozincates were converted easily and in high yield to the iodides. The acid form of the *racemic* glycine carboxylato-*O,O* bridged complex was isolated as the bromide, Δ,Δ-and Λ,Λ-[(en)$_2$Cr(glyH)(OH)Cr(en)$_2$]Br$_5$.3H$_2$O. This salt was easily converted to the deprotonated form, isolated as the bromide, Δ,Δ- and Λ,Λ-[(en)$_2$-Cr(gly)(OH)Cr(en)$_2$]Br$_4$.4H$_2$O.

Structure assignments. The chemical properties of these new binuclear complexes provided unambiguous evidence for a common carboxylato-*O,O* bridged structure:
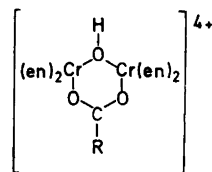
For each carboxylate bridge the pair of isomers, Δ,Λ and (Δ,Δ- and Λ,Λ), had very similar properties (visible spectra, infrared spectra and acid-base properties), but X-ray powder diffraction digrams showed unambiguously that different isomers had been formed, *e.g.*, powder diagrams of the two salts Δ,Λ-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$.H$_2$O and Δ,Δ- and Λ,Λ-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$.-H$_2$O were clearly different. The assignments of configuration, Δ and Λ, have therefore been made according to the configurations of the parent diols.

The visible absorption spectra showed practically no dependence on [H$^+$] in the region $10^{-9} \leq$ [H$^+$] ≤ 1 M. This clearly excluded structures having terminal aqua or hydroxo groups and thereby provided strong evidence for the proposed structures. The μ-acetato and μ-formato compounds reacted neutral and showed no buffer capacity in the region $4 \leq pH \leq 10$ as indicated by glass-electrode measurements.

The complexes with glycine reacted nearly neutral

Table 1. Spectral data for Δ,Λ and (Δ,Δ- and Λ,Λ) isomers in 0.01 M HCl at 25 °C.

Cation	Δ,Λ Isomer		Δ,Δ- and Λ,Λ Isomers	
	$(\varepsilon,\lambda)_{max}$	$(\varepsilon,\lambda)_{max}$	$(\varepsilon,\lambda)_{max}$	$(\varepsilon,\lambda)_{max}$
$[(en)_2Cr(ac)(OH)Cr(en)_2]^{4+}$	(210, 505)	(98.6, 378)	(202, 505)	(97.4, 377)
$[(en)_2Cr(form)(OH)Cr(en)_2]^{4+}$	(202, 504)	(89.7, 376)	(194, 504)	(88.2, 376)
$[(en)_2Cr(glyH)(OH)Cr(en)_2]^{5+}$	(206, 504)	(84.3, 374)	(192, 505)	(83.4, 374)

but showed buffer capacity in the region pH 7−8 due to the base properties of the glycine amino group (*vide infra*). The observation that the glycinato complexes showed very small spectral changes in this pH region is in agreement with the proposed structures since deprotonation of an ammonium group which is remote from the Cr(III) centres should only influence the visible absorption spectra to a small extent.

The visible absorption spectra of all the complexes are nearly identical (Table 1) despite the great difference in basicity of the carboxylate ligands, and this supports the proposed common structure. The same feature[1,3,4] has been observed previously for the carboxylato bridged complexes $[(NH_3)_4Co-(RCOO)(NH_2)Co(NH_3)_4]^{4+}$ and $[(NH_3)_3Co-(RCOO)(OH)_2Co(NH_3)_3]^{3+}$.

From the data in Table 1 the Δ value for the carboxylato bridged chromium(III) complexes is calculated as 19.82 kK. This value is close to the Δ value determined[8] for the complex Δ,Λ-$[(H_2O)-(en)_2Cr(OH)Cr(en)_2(H_2O)]^{5+}$ (Δ = 19.88 kK). The result is consistent with the observation that carboxylate and water have nearly the same position in the spectrochemical series.[14]

The proposed common structures were further supported by infrared spectroscopy data as discussed below.

Infrared spectra. Many investigators have discussed the vibrational spectra of metal formates and acetates, and found that the antisymmetric carboxylate stretching frequency $\nu_{as}(CO)$ is most sensitive to change in the metal.[1,4,15] In the carboxylato bridged binuclear cobalt(III) complexes the frequencies $\nu_{as}(CO)$ are shifted 20−50 cm^{-1} to lower frequency compared to the free carboxylates.[1,4] The present binuclear chromium complexes show a similar shift in $\nu_{as}(CO)$ (21 to 28 cm^{-1}). Nakamoto has demonstrated that the separation Δ*ν* between the antisymmetric and symmetric stretching frequencies in carboxylato complexes reflects the type of bonding.[15] It was shown that

Δ*ν* for a given carboxylic acid decreases in the order: monodentate-bound carboxylate, free carboxylate and bidentate or bridged carboxylate. These general features are illustrated in Table 2, which compares literature data for some cobalt(III) complexes whose structures are now well established.[1,4] The relevant data for acetato and formato complexes studied in this work are also shown in Table 2. It is seen that the Δ*ν* values for all the compounds are lower than those for the corresponding free carboxylate ions, and this clearly supports the proposed structures and also excludes a bridged structure with only one carboxylate oxygen coordinated to both chromium(III) atoms. With the latter structure one would except a higher value of Δ*ν*.

Weighardt has demonstrated a linear correlation between the pK_a values of the free carboxylic acids and the frequencies $\nu_{as}(CO)$ of the corresponding *μ*-carboxylato-di-*μ*-hydroxo binuclear cobalt(III) complexes.[4] A similar linear relationship apparently holds for *μ*-carboxylato-*μ*-hydroxo binuclear chromium(III) complexes, as shown in Fig. 1. The possibility of determining some otherwise inaccessible acidity constants therefore exists, as discussed below for glycine. Using the frequencies $\nu_{as}(CO)$ for the Δ,Λ and the (Δ,Δ- and Λ,Λ) isomers of $[(en)_2Cr-(gly)(OH)Cr(en)_2]Br_4.4H_2O$ together with the corresponding linear relationships (Fig. 1), an estimate of the microscopic acid dissociation constant, K_{a3}, for glycine defined by the equilibrium

$$H_2N\ CH_2\ COOH \overset{K_{a3}}{=\!=\!=} H_2NCH_2COO^- + H^+$$
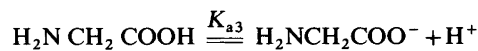
is possible. These estimates gave the value pK_{a3} = 4.28 ± 0.1 (*I* = 0, 25 °C) (Fig. 1). Combination of this value with the macroscopic acid dissociation constants for glycine,[17] pK_{a1} = 2.36 and pK_{a2} = 9.91, therefore yields the microscopic equilibrium constants K_{a4} and K_{eq} defined by the equilibria

Table 2. A comparison of antisymmetrical and symmetrical $C-O$ stretching frequencies (cm^{-1}) and the separation of these bands (Δv).

Compound	$v_{as}(CO)$	$v_{s}(CO)$	Δv	Ref.
Na(CH$_3$COO)	1578	1425	153	15
[Co(NH$_3$)$_5$(CH$_3$COO)](ClO$_4$)$_2$	1603	1380	223	1
[(NH$_3$)$_4$Co(CH$_3$COO)(NH$_2$)Co(NH$_3$)$_4$]Cl$_4$.2H$_2$O	1530	1410	120	1
Δ,Λ-[(en)$_2$Cr(CH$_3$COO)(OH)Cr(en)$_2$](ClO$_4$)$_4$.2H$_2$O	1552	1418	134	This work
(Δ,Δ- and Λ,Λ)-[(en)$_2$Cr(CH$_3$COO)(OH)Cr(en)$_2$]I$_4$.H$_2$O	1550	1414	136	This work
Na(HCOO)	1590	1355	235	1
[Co(NH$_3$)$_5$(HCOO)]Br$_2$	1640	1345	295	1
[(NH$_3$)$_4$Co(HCOO)(NH$_2$)Co(NH$_3$)$_4$]Cl$_4$.4H$_2$O	1570	1365	205	1
Δ,Λ-[(en)$_2$Cr(HCOO)(OH)Cr(en)$_2$](ClO$_4$)$_4$	1569	1379	190	This work
(Δ,Δ- and Λ,Λ)-[(en)$_2$Cr(HCOO)(OH)Cr(en)$_2$]I$_4$.2H$_2$O	1569	1376	193	This work
Δ,Λ-[(en)$_2$Cr(NH$_3$CH$_2$COO)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$Cl.4H$_2$O	1602	1414	188	This work
(Δ,Δ- and Λ,Λ)-[(en)$_2$Cr(NH$_3$CH$_2$COO)(OH)Cr(en)$_2$]Br$_5$.3H$_2$O	1598	1413	185	This work
Δ,Λ-[(en)$_2$Cr(NH$_2$CH$_2$COO)(OH)Cr(en)$_2$]Br$_4$.4H$_2$O	1561	1409	152	This work
(Δ,Δ- and Λ,Λ)-[(en)$_2$Cr(NH$_2$CH$_2$COO)(OH)Cr(en)$_2$]Br$_4$.4H$_2$O	1559	1403	156	This work

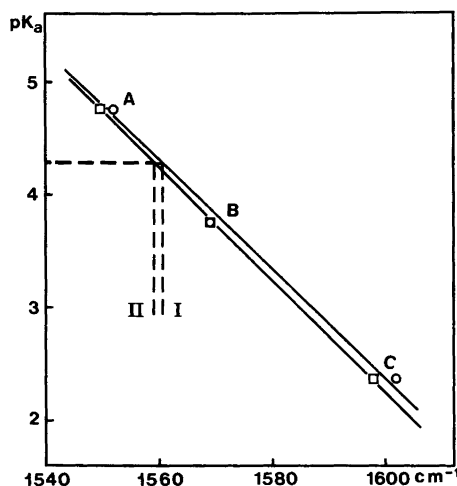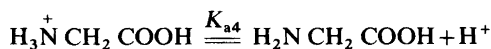*Fig. 1.* Plot of $v_{as}(CO)$ stretching frequency of the bridging carboxylate groups against pK_a values of the free carboxylic acids, (A) CH$_3$COOH (pK_a 4.76), (B) HCOOH (pK_a 3.75), (C) $^+$H$_3$NCH$_2$COOH (pK_a 2.36);[17] $\bigcirc$, Δ,Λ-μ-carboxylato-μ-hydroxo-bis[bis(ethylenediamine)chromium(III)] complexes; $\square$, (Δ,Δ- and Λ,Λ)-μ-carboxylato-μ-hydroxo-bis-[bis(ethylenediamine)chromium(III)] complexes. Dotted lines: Determination of the microscopic acid dissociation constant, K_{a3}, of glycine from the values of $v_{as}(CO)$ of the aminoacetato bridged complexes for the Δ,Λ isomer (I) and the (Δ,Δ- and Λ,Λ) isomers(II), respectively.

$$H_3\overset{+}{N}\,CH_2\,COOH \xrightleftharpoons{K_{a4}} H_2N\,CH_2\,COOH + H^+$$

$$H_2N\,CH_2\,COOH \xrightleftharpoons{K_{eq}} {}^+H_3N\,CH_2\,COO^-$$

We thus obtain the values $pK_{a4} = 7.99 \pm 0.1$ and $K_{eq} = 4.3 \times 10^5$ ($I = 0$, 25 °C). These microscopic dissociation constants have never been determined previously, but the proposal[16] that the acid dissociation constant for glycine ethyl ester ($pK_a = 7.75$, 0.1 M NaNO$_3$, 25 °C)[17] can be taken as a good estimate of the magnitude of K_{a4} is seen to agree with the present data.

Protolytic properties of the complexes. The acid dissociation constants, K_a, of the glycinato bridged complexes were determined potentiometrically in 1.0 M NaClO$_4$ (20 °C) for both isomers.
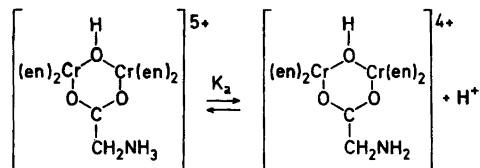
Because of the carboxylato bridge cleavage reaction (*vide infra*) a normal acidometric titration could not be performed. Therefore buffer solutions of [(en)$_2$Cr(gly)(OH)Cr(en)$_2$]$^{4+}$ and [(en)$_2$Cr(glyH)(OH)Cr(en)$_2$]$^{5+}$ in 1.0 M NaClO$_4$ were made

as rapid as possible and pH at the time of dissolution was obtained by extrapolation. For each isomer pK_a was obtained as the average of 5 determinations and the values for the Δ,Λ and (Δ,Δ- and Λ,Λ) isomers, respectively, were 7.46 ± 0.05 and 7.59 ± 0.05. The pK_a value for free glycine in the same medium is 9.76[17] and coordination to the two chromium(III) centres has therefore increased the acid strength considerably. A much smaller increase in the acid strength has been observed for the complex ion $[Co(NH_3)_5OCOCH_2NH_3]^{3+}$ ($pK_a = 8.5, I = 0.03$ M, 25 °C).[18]

When strong base is added to aqueous solutions of the carboxylato bridged complexes, the colour instantaneously changes from red to blue. The reactions are reversible and are presumably due to deprotonation of the hydroxo bridges giving *μ*-carboxylato-*μ*-oxo cations ($pK_a \simeq 12$). Similar acid properties have recently been reported for the ammonia diol,[19] $[(NH_3)_4Cr(OH)_2Cr(NH_3)_4]^{4+}$, the *meso* and *racemic* isomers of the ethylenediamine diol,[8,9] $[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$, and for the sulfato bridged complex, Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2]^{3+}$.[5] In all these compounds the hydroxo bridge forms have $pK_a \simeq 12$ and the oxo bridged forms are blue.

Kinetic data. The reactions between *meso* or *racemic* diol and these carboxylic acids were followed spectrophotometrically. For each reaction the final spectra were very similar to those of the corresponding authentic carboxylato bridged complexes, suggesting that the reactions are essentially quantitative. The pseudo first-order rate constants for the reactions of *meso* diol in 4 M CH_3COOH, 4 M $HCOOH$ and 4 M $Cl^-,^+H_3NCH_2COOH$, respectively, were $(5 \pm 1) \times 10^{-4}$ s^{-1}, $(7 \pm 0.3) \times 10^{-4}$ s^{-1}, and $(8 \pm 3) \times 10^{-5}$ s^{-1}. The rate constants for the reactions of the *racemic* diol were, within experimental error, identical to the respective values for the *meso* diol. These reactions are much slower than the equilibration reactions between diol and monools,[8,9] and equilibrium between diol and monools is therefore maintained throughout after an induction period. The induction period observed in the early stages of each reaction corresponds to the time needed to establish diol-monool equilibrium, although a simultaneous pre-equilibrium involving a non-bridging carboxylate, $[(H_2O)(en)_2Cr(OH)Cr(en)_2(OOCR)]^{4+}$, is also likely to be involved.

Base hydrolysis. These new dimers are robust in acid solution but as the pH is increased the carboxylato bridge is cleaved rather fast, as discussed in the following for the Δ,Λ isomers. In 1 M NaOH the blue *μ*-carboxylato-*μ*-oxo ions, discussed above, decompose giving reddish-purple products. The hydrolysis at 25 °C is fairly rapid for the acetato and glycinato complexes ($t_{\frac{1}{2}} \simeq 5$ min) and very fast for the formato complex ($t_{\frac{1}{2}} \simeq 1$ s). A major part of the hydrolysis process was shown to be carboxylato bridge cleavage giving monool, Δ,Λ-$[(OH)(en)_2Cr(OH)Cr(en)_2(OH)]^{3+}$. Thus, by acidifying the product solutions it was possible to isolate re-formed *meso* diol as the tetrachlorozincate (*ca.* 30 %). At pH 8 the hydrolysis is much slower and under these conditions the acetato complex appears to be much more robust ($t_{\frac{1}{2}} \simeq 10$ h) than the formato and glycinato complexes ($t_{\frac{1}{2}} \simeq 1$ h), as indicated by spectrophotometric measurements at 25 °C (1 M NH_4Cl, 0.1 M NH_3). These data indicate that the robustness of these carboxylato bridged complexes increases as pK_a of the corresponding acid increases, which is a reasonable result.

EXPERIMENTAL

Materials. Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$, Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]Cl_4 \cdot 2H_2O$ and Δ,Δ- and Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4 \cdot H_2O$ were prepared as described in literature.[19,9] All other materials were of analytical grade.

Analysis. Cr analyses were determined by atomic absorption spectrophotometry by Karen Jørgensen at Chemistry Department I, H. C. Ørsted Institute, and C, H, N, Cl, Br and I analyses were made by the microanalytical laboratory at the same institute.

Instruments. A Zeiss DMR 21 spectrophotometer or a Beckman Spectrophotometer Acta III were used for spectrophotometric measurements in the visible region. For the spectrophotometric data given below the absorptivity ε has been given in 1 mol^{-1} cm^{-1} and the wavelength λ has been given in nm. Infrared spectra of the compounds in potassium bromide discs were recorded on a Perkin-Elmer 580 infrared spectrophotometer.

The pH-measurements were made with a GK 2301 C combined glass and calomel electrode connected to a PHM 52 digital pH-meter, all from Radiometer, Copenhagen. The saturated potassium chloride calomel electrode was modified to 1 M sodium chloride in order to avoid precipitation of $KClO_4$ in the boundary between the medium and the electrode.

Guinier powder diffraction diagrams were measured with a Guinier powder camera with Cu$K\alpha$ radiation.

Preparations. 1. Δ,Λ-μ-Acetato-μ-hydroxobis[bis-(ethylenediamine)chromium(III)]   tetrachlorozincate. Δ,Λ-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$.H$_2$O. A solution of Δ,Λ-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_4$ (10 g, 12.9 mmol) in 4 M acetic acid (125 ml) was kept at 24 °C for 6 h and the colour changed from reddish-purple to red. Addition of 4 M Li$_2$ZnCl$_4$ (25 ml) gave precipitation of nice red crystals of Δ,Λ-[(en)$_2$-Cr(ac)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$.H$_2$O. The crystals were filtered off, washed thoroughly with 96 % ethanol and then with ether. The product was dried in air. Yield 7.6 g (69 %). The crude product (4 g) was dissolved in 0.01 M hydrochloric acid (45 ml) and then 4 M Li$_2$ZnCl$_4$ (10 ml) was added to the filtered solution. The precipitate was isolated as above. Yield 4.0 g (100 %). This product was pure. Anal. [Cr$_2$(C$_2$H$_8$N$_2$)$_4$(OH)(C$_2$H$_3$O$_2$)](ZnCl$_4$)$_2$.H$_2$O: Cr, C, N, H, Cl. Spectral data in 0.01 M hydrochloric acid: $(\varepsilon,\lambda)_{max} = (211, 505.5)$, $(98.9, 378)$; $(\varepsilon,\lambda)_{min} = (44.7, 431)$.

2. Δ,Λ-μ-Acetato-μ-hydroxobis[bis(ethylenedi-amine)chromium(III)]perchlorate. Δ,Λ-[(en)$_2$Cr-(ac)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$.H$_2$O (5 g, 5.86 mmol) was dissolved in 0.01 M perchloric acid (50 ml) and the filtered solution was precipitated by addition of a saturated solution of sodium perchlorate (100 ml). The precipitate was filtered off and washed thoroughly with 96 % ethanol and then with ether. The product was dried in air. Yield 4.1 g (82 %). The crude product (2.0 g) was dissolved in 0.01 M perchloric acid (10 ml) and a saturated solution of sodium perchlorate (20 ml) was then added to the filtered solution. The precipitate was isolated as above. Yield 1.7 g (85 %). This product was pure. Anal. [Cr$_2$(C$_2$H$_8$N$_2$)$_4$(OH)(C$_2$H$_3$O$_2$)]-(ClO$_4$)$_4$.2H$_2$O: Cr, C, N, H, Cl. Spectral data; medium: 1.0 M hydrochloric acid; $(\varepsilon,\lambda)_{max} = (212, 506)$, $(100, 378)$; $(\varepsilon,\lambda)_{min} = (43.8, 431)$; medium: 0.01 M HCl; $(\varepsilon,\lambda)_{max} = (209, 505.5)$, $(98.4, 377.5)$; $(\varepsilon,\lambda)_{min} = (44.0, 431)$; medium: 0.1 M ammonia, 0.1 M ammonium chloride; $(\varepsilon,\lambda)_{max} = (206, 506)$, $(99.6, 376)$; $(\varepsilon,\lambda)_{min} = (45.0, 431)$.

3. (Δ,Δ- and Λ,Λ)-μ-Acetato-μ-hydroxobis[bis-(ethylenediamine)chromium(III)]   tetrachlorozin-cate. Δ,Δ- and Λ,Λ-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$]-(ZnCl$_4$)$_2$.H$_2$O. Pure Δ,Δ- and Λ,Λ-[(H$_2$O)(en)$_2$Cr-(OH)Cr(en)$_2$(OH)]Br$_4$.H$_2$O (3 g, 4.09 mmol) was dissolved in 0.5 M sodium hydroxide (8 ml) and then 4 M acetic acid (8 ml) was added rapidly. This gave a saturated solution of the aquahydroxo monool (which otherwise dissolves slowly in 4 M acetic acid) and a partial reprecipitation of the bromide salt. The suspension was stirred at 20 °C for 18 h during which time the precipitate dissolved. 4 M Li$_2$ZnCl$_4$ (12 ml) was added and by scratching with a glass rod the product precipitated. The mixture was filtered after cooling in ice for 15 min. The product was washed with cold 50 % ethanol

(10 ml) and two portions of 96 % ethanol (10 ml). Drying in air yielded 2.5 g (72 %). The crude product was dissolved in water (20 ml) and to the filtered solution was added concentrated hydrochloric acid (0.2 ml) and 4 M Li$_2$ZnCl$_4$ (4 ml). The mixture was cooled in ice for 15 min and filtered. The product was washed as above. Yield 2.2 g (88 %). This product was pure. Anal. [Cr$_2$(C$_2$H$_8$N$_2$)$_4$-(OH)(C$_2$H$_3$O$_2$)](ZnCl$_4$)$_2$.H$_2$O: Cr, C, H, N, Cl. Spectral data in 0.01 M hydrochloric acid; $(\varepsilon,\lambda)_{max} = (202, 505)$, $(96.7, 378)$; $(\varepsilon,\lambda)_{min} = (42.8, 430)$.

4. (Δ,Δ- and Λ,Λ)-μ-Acetato-μ-hydroxobis[bis-(ethylenediamine)chromium(III)] iodide. Δ,Δ- and Λ,Λ-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$]I$_4$.H$_2$O. Pure Δ,Δ- and Λ,Λ-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$.H$_2$O (2 g, 2.37 mmol) was added to 6 M sodium iodide (8 ml) and the suspension was kept at room temperature with stirring for 1 h. In this way red crystals of the iodide salt separated almost quantitatively. The mixture was filtered and washed once with icecold water (5 ml). The product was dissolved in water (15 ml) and reprecipitated with 6 M sodium iodide (5 ml). After cooling for half an hour the sample was filtered off, washed with icecold water (5 ml) and then two portions of 96 % ethanol (5 ml). Drying in air yielded 1.8 g (79 %). This product was pure. Anal. [Cr$_2$(C$_2$H$_8$N$_2$)$_4$(OH)(C$_2$H$_3$O$_2$)]I$_4$.H$_2$O: Cr, C, H, N, Cl. Spectral data; medium: 0.01 M hydrochloric acid; $(\varepsilon,\lambda)_{max} = (203, 505)$, $(98.1, 377)$; $(\varepsilon,\lambda)_{min} = (42.3, 430)$; medium 0.1 M ammonia, 0.9 ammonium chloride; $(\varepsilon,\lambda)_{max} = (197, 505)$, $(94.8, 377)$; $(\varepsilon,\lambda)_{min} = (42.3, 430)$.

5. Δ,Λ-μ-Formato-μ-hydroxobis[bis(ethylenedi-amine)chromium(III)]   tetrachlorozincate. Δ,Λ-[(en)$_2$Cr(form)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$. A solution of Δ,Λ-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_4$ (5 g, 6.45 mmol) in 2 M formic acid (50 ml) was kept at 23 °C for 20 h, during which time the colour of the solution changed from reddish-purple to red. The solution was filtered and 4 M Li$_2$ZnCl$_4$ (10 ml) was then added. Nice red crystals of Δ,Λ-[(en)$_2$Cr(form)(OH)Cr-(en)$_2$](ZnCl$_4$)$_2$ precipitated. The crystals were filtered off and washed thoroughly with 96 % ethanol and then with ether. The product was dried in air. Yield 3.3 g (62 %). The crude product (1.0 g) was dissolved in 0.01 M hydrochloric acid (10 ml) and 4 M Li$_2$ZnCl$_4$ (5 ml) was then added to the filtered solution. The crystals were isolated as above. Yield 0.92 g (92 %). This product was pure. Anal. [Cr$_2$(C$_2$H$_8$N$_2$)$_4$(OH)(CHO$_2$)](ZnCl$_4$)$_2$: Cr, C, N, H, Cl. Spectral data in 0.01 M hydrochloric acid: $(\varepsilon,\lambda)_{max} = (200, 504)$, $(88.6, 376.5)$; $(\varepsilon,\lambda)_{min} = (47.5, 431)$.

6. Δ,Λ-μ-Formato-μ-hydroxobis[bis(ethylenedi-amine)chromium(III)] perchlorate. Δ,Λ-[(en)$_2$Cr-(form)(OH)Cr(en)$_2$](ClO$_4$)$_4$. Pure Δ,Λ-[(en)$_2$Cr-(OH)$_2$Cr(en)$_2$](ClO$_4$)$_4$ (5 g, 6.45 mmol) was reacted with 2 M formic acid (50 ml) as described in preparation No. 5, and thereafter solid sodium

perchlorate (50 g) was added to the filtered solution. Red crystals of the perchlorate salt precipitated. The crystals were filtered off and washed thoroughly with 96 % ethanol and then with ether. The product was dried in air. Yield 2.3 g (44 %). The crude product (2.0 g) was dissolved in 0.01 M perchloric acid (12 ml) and then a saturated solution of sodium perchlorate (12 ml) was added to the filtered solution. The precipitate was isolated as above. Yield 1.52 g (76 %). This product was pure. Anal. $[Cr_2(C_2H_8N_2)_4(OH)(CHO_2)](ClO_4)_4$: Cr, C, N, H, Cl. Spectral data; medium: 1.0 M hydrochloric acid: $(\varepsilon,\lambda)_{max} = (202, 505), (92.0, 375.5); (\varepsilon,\lambda)_{min} = (47.8, 431)$; medium: 0.01 M hydrochloric acid: $(\varepsilon,\lambda)_{max} = (204, 505); (91.0, 376.5); (\varepsilon,\lambda)_{min} = (48.4, 431)$; medium $= 0.1$ M ammonia, 0.1 M ammonium chloride: $(\varepsilon,\lambda)_{max} = (195, 505), (94.0, 375); (\varepsilon,\lambda)_{min} = (49.6, 431)$.

7. *(Δ,Δ- and Λ,Λ)-μ-Formato-μ-hydroxobis[bis-(ethylenediamine)chromium(III)]   tetrachlorozincate.* Δ,Δ- and Λ,Λ-[(en)₂Cr(form)(OH)Cr(en)₂]-$(ZnCl_4)_2$. Pure $(Δ,Δ-$ and $Λ,Λ)$-$[(H_2O)(en)_2Cr-(OH)Cr(en)_2(OH)]Br_4.H_2O$ (3 g, 4.09 mmol) was added to 0.5 M sodium hydroxide (8 ml), and the solution was rapidly added to concentrated formic acid (3 ml). After stirring at 20 °C for 18 h 4 M Li_2ZnCl_4 (10 ml) was added, and by scratching with a glass rod the product precipitated. The mixture was filtered after cooling in ice for 15 min. The product was washed with cold 50 % ethanol (10 ml) and two portions of 96 % ethanol (10 ml). Drying in air yielded 1.5 g (44 %).

The crude product was dissolved in water (10 ml) and to the filtered solution was added concentrated hydrochloric acid (0.1 ml) and 4 M Li_2ZnCl_4 (2 ml). The mixture was cooled in ice for 15 min and filtered. The product was washed as above. Yield 1.0 g (67 %). This product was pure. Anal. $[Cr_2(C_2H_8N_2)_4-(OH)(CHO_2)](ZnCl_4)_2$: Cr, C, H, N, Cl. Spectral data in 0.01 M hydrochloric acid; $(\varepsilon,\lambda)_{max} = (193, 504), (87.9, 376); (\varepsilon,\lambda)_{min} = (43.8, 430)$.

8. *(Δ,Δ- and Λ,Λ)-μ-Formato-μ-hydroxobis[bis-(ethylenediamine)chromium(III)] iodide.* Δ,Δ- and Λ,Λ-[(en)₂Cr(form)(OH)Cr(en)₂]I₄.2H₂O. This salt was prepared in the same way as the Δ,Δ- and Λ,Λ-*μ*-acetato iodide salt, preparation No. 4. Yield: 1.7 g (75 %). Anal. $[Cr_2(C_2H_8N_2)_4(OH)(CHO_2)]-I_4.2H_2O$: Cr, C, H, N, I. Spectral data; medium: 0.01 M hydrochloric acid; $(\varepsilon,\lambda)_{max} = (194, 504), (88.4, 376); (\varepsilon,\lambda)_{min} = (45.9, 430)$; medium: 0.1 M ammonia, 0.9 M ammonium chloride; $(\varepsilon,\lambda)_{max} = (196, 504), (86.7, 376); (\varepsilon,\lambda)_{min} = (44.0, 430)$.

9. *Δ,Λ-μ-Ammonioacetato-μ-hydroxobis[bis(ethylenediamine)chromium(III)]   tetrachlorozincate.* Δ,Λ-[(en)₂Cr(glyH)(OH)Cr(en)₂](ZnCl₄)₂Cl.4H₂O. To a solution of glycine (1.13 g, 15 mmol) in 1 M hydrochloric acid (25 ml) at 55 °C was added Δ,Λ-[(en)₂Cr(OH)₂Cr(en)₂]Cl₄.2H₂O (5 g, 9.0 mmol).

The chloride dissolved within minutes and the solution was kept at 55 °C for half an hour. The solution was then cooled in ice and 4 M Li_2ZnCl_4 (12 ml) was added slowly to the cold solution. Red crystals of the glycinato complex precipitated. The crystals were filtered off and washed thoroughly with 96 % ethanol and then with ether. Drying in air gave 2.7 g (31 %). The crude salt (2 g) was dissolved in 0.01 M hydrochloric acid (10 ml) at room temperature. The solution was filtered, cooled with ice and then 4 M Li_2ZnCl_4 (5 ml) was added slowly. The precipitate was isolated as above. Yield 1.62 g (81 %). This product was pure. Anal. $[Cr_2(C_2H_8N_2)_4(OH)(C_2H_5NO_2)](ZnCl_4)_2.Cl.4H_2O$: C, N, H, Cl. Spectral data; medium: 1.0 M hydrochloric acid: $(\varepsilon,\lambda)_{max} = (209, 504), (85.6, 375); (\varepsilon,\lambda)_{min} = (54.2, 431)$. Medium: 0.01 M hydrochloric acid: $(\varepsilon,\lambda)_{max} = (206, 504.5), (84.3, 374); (\varepsilon,\lambda)_{min} = (53.3, 431)$. Medium: 0.1 M ammonia, 0.1 M ammonium chloride: $(\varepsilon,\lambda)_{max} = (206, 505.2), (98.4, 375.5); (\varepsilon,\lambda)_{min} = (41.2, 431)$.

10. *Δ,Λ-μ-Aminoacetato-μ-hydroxobis[bis(ethylenediamine)chromium(III)] bromide.* Δ,Λ-[(en)₂Cr(gly)(OH)Cr(en)₂]Br₄.4H₂O. Pure Δ,Λ-[(en)₂Cr-(glyH)(OH)Cr(en)₂](ZnCl₄)₂Cl.4H₂O (5.4 g, 5.63 mmol) was dissolved in ice-cold 2 M sodium hydroxide (15 ml). After some minutes a white precipitate of zinc hydroxide was filtered off and a saturated solution of sodium bromide (6 ml) was added to the filtrate while cooled in ice. Red crystals of the bromide precipitated. The precipitate was filtered off, washed with 96 % ethanol, then ether and dried in air. Yield 2.1 g (45 %). The crude bromide (1.8 g) was dissolved at 20 °C in water (10 ml) and a saturated solution of sodium bromide (5 ml) was then added to the filtered solution. The precipitate was isolated as above. Yield 1.49 g (83 %) of a pure product. Anal. $[Cr_2(C_2H_8N_2)_4(OH)(C_2H_4NO_2)]Br_4.4H_2O$: C, N, H, Br. Spectral data in 0.01 M hydrochloric acid: $(\varepsilon,\lambda)_{max} = (206, 505), (84.2, 374); (\varepsilon,\lambda)_{min} = (53.8, 431)$.

11. *Δ,Δ- and Λ,Λ-μ-Ammonioacetato-μ-hydroxobis[bis(ethylenediamine)chromium(III)] bromide.* Δ,Δ- and Λ,Λ-[(en)₂Cr(glyH)(OH)Cr(en)₂]Br₅-3H₂O. Pure Δ,Δ- and Λ,Λ-[(H₂O)(en)₂Cr(OH)Cr-(en)₂(OH)]Br₄.H₂O (3 g, 4.09 mmol) was added to a solution of glycine (3.5 g, 46.6 mmol) in water (10 ml) at 34−36 °C with stirring. When the solution was clear concentrated hydrobromic acid (2 ml) was added dropwise. The solution was kept at 34−36 °C for 15 min. To the resulting solution was added a saturated solution of sodium bromide (3 ml) and ethanol (3 ml) and the solution was cooled in ice for half an hour. The red precipitate was filtered off and washed with 96 % ethanol. Drying in air yielded 2.3 g (63 %). The crude product was reprecipitated from water. Anal. $[Cr_2(C_2H_8N_2)_4-(OH)(C_2H_5NO_2)]Br_5.3H_2O$: Cr, C, H, N, Br.

Spectral data: Medium: 0.01 M hydrochloric acid; $(\varepsilon,\lambda)_{max} = (191, 504)$, $(84.4, 374)$; $(\varepsilon,\lambda)_{min} = (50.0, 430)$; medium: 0.1 M ammonia, 0.9 M ammonium chloride; $(\varepsilon,\lambda)_{max} = (192, 505)$, $(94, 374)$; $(\varepsilon,\lambda)_{min} = (44.8, 430)$.

12. (Δ,Δ- and Λ,Λ)-μ-Aminoacetato-μ-hydroxobis-[bis(ethylenediamine)chromium(III)] bromide. Δ,Δ- and Λ,Λ-[(en)$_2$Cr(gly)(OH)Cr(en)$_2$]Br$_4$.4H$_2$O. Pure (Δ,Δ- and Λ,Λ)-[(en)$_2$Cr(glyH)(OH)Cr(en)$_2$]Br$_5$.-3H$_2$O (1.0 g, 1.12 mmol) was dissolved in water (5 ml). The solution was cooled in ice and 12 M ammonia (1 ml) and sodium bromide (1 g) was added rapidly. The solution was cooled for another 5 min and the precipitate was filtered off. The red product was washed once with cold 50 % ethanol, twice with 96 % ethanol, and then dried in air. Yield 0.7 g (76 %). Anal. [Cr$_2$(C$_2$H$_8$N$_2$)$_4$(OH)-(C$_2$H$_4$NO$_2$)]Br$_4$.4H$_2$O: Cr, C, H, N, Br. Spectral data in 1.0 M hydrochloric acid; $(\varepsilon,\lambda)_{max} = (192, 505)$, $(82.4, 375)$; $(\varepsilon,\lambda)_{min} = (50.5, 431)$.

Powder diagrams. Guinier X-ray powder diagrams of the Δ,Λ isomers of [(en)$_2$Cr(ac)(OH)Cr(en)$_2$]-(ZnCl$_4$)$_2$.H$_2$O, [(en)$_2$Cr(form)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$ and [(en)$_2$Cr(gly)(OH)Cr(en)$_2$]Br$_4$.4H$_2$O were clearly different from those of their respective (Δ,Δ- and Λ,Λ) isomers.

Potentiometric determination of the acid dissociation constants of the glycine complexes. Solutions of Δ,Λ-[(en)$_2$Cr(gly)(OH)Cr(en)$_2$]Br$_4$.4H$_2$O (2.8×10^{-3} -5.3×10^{-3} M) in 2.5×10^{-3} M HClO$_4$, 1.00 M NaClO$_4$ at 20 °C were made by dissolving the salt as rapidly as possible in a thermostated measuring vessel with stirring and N$_2$-bubbling. Solutions of Δ,Δ- and Λ,Λ-[(en)$_2$Cr(OH)(glyH)Cr(en)$_2$]Br$_5$.-3H$_2$O (3.0×10^{-3} -5.4×10^{-3} M) in 2.5×10^{-3} M NaOH, 1 M NaClO$_4$ were made similarly. Reliable readings on the pH-meter could be obtained 30 s after the time of dissolution. The measurements were continued over a period of 10 min and the pH at the time of dissolution was then calculated by extrapolation. The definition pH $\equiv \log[\text{H}^+]$ was employed throughout, and concentration pH standards were made in the actual salt medium.

Deuterated complexes. Deuterated complexes of the carboxylato bridged chromium(III) complexes listed in Table 2 were made as follows. Bromides, iodides or perchlorates were dissolved in D$_2$O at 0-5 °C and the solutions were then made basic (pH $\simeq$ 10-11) with 1 M NaOD in D$_2$O. After 30 to 60 s the solutions were then acidified with a small excess of 12 M hydrobromic acid or 12 M perchloric acid (in water). From the acidified solutions the deuterated complex salts were then precipitated essentially by following the individual procedures given above. Deuterated salts of [(en)$_2$Cr(gly)(OH)-Cr(en)$_2$]Br$_4$.4H$_2$O were isolated directly from the basic solutions. Deuterated Δ,Λ-[(en)$_2$Cr(glyH)-(OH)Cr(en)$_2$](ZnCl$_4$)$_2$Cl.4H$_2$O was made similarly,

but now the D$_2$O solution was made basic using excess of potassium carbonate.

Kinetic measurements. The formation of each of the six μ-carboxylato-μ-hydroxo complexes was studied at 25 °C by following the change of the absorbancy in the region 650-350 nm of 3×10^{-3} M solutions of *meso* diol perchlorate or *racemic* monool bromide in 4 M RCOOH (R=CH$_3$-, H- and Cl$^-$, $^+$H$_3$NCH$_2$ -). All kinetic measurements were made under pseudo first-order conditions, *i.e.*, the change of the carboxylic acid and of the hydrogen ion concentration during a kinetic run was never greater than 0.1 %. For each kinetic run three isosbestic points were observed. Final constant spectra were obtained after 3-12 h and were similar to those of the corresponding authentic μ-carboxylato-μ-hydroxo complexes. Pseudo first-order rate constants were obtained from plots of $\log(\text{OD}_t - \text{OD}_\infty)$ *vs.* time for the wavelengths $\lambda = 560$ and 500 nm. These plots were for the acetate and formate reactions linear for three half-lives, but for the acetate reactions a slight dependence on the wavelength was observed. In each experiment a short induction period (2-5 min) preceded the period for which first-order conditions were observed. For the reactions with glycine curvatures were observed during the entire reaction, and only an approximate over-all rate constant has therefore been obtained.

Carboxylato bridge cleavage. Conversion of Δ,Λ-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$.H$_2$O to Δ,Λ diol tetrachlorozincate was established *via* base hydrolysis as follows: Δ,Λ-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$]-(ZnCl$_4$)$_2$.H$_2$O (0.200 g, 0.23 mmol) was dissolved in 2 M sodium hydroxide (1 ml), and after half an hour at 25 °C the solution had changed colour from blue to reddish-purple. The solution was cooled in ice and acidified to pH 6 with 12 M hydrochloric acid. The solution was then left at 25 °C, and within minutes purple crystals of Δ,Λ diol tetrachlorozincate precipitated. In order to complete the precipitation 4 M Li$_2$ZnCl$_4$ (0.5 ml) was added. The precipitate was filtered off, washed with 96 % ethanol, ether and then dried in air. Yield 65 mg (33 %). This product was identified as Δ,Λ diol by comparing its infrared spectrum with that of an authentic sample. Following the procedure above conversion of Δ,Λ-[(en)$_2$(glyH)(OH)Cr(en)$_2$]-(ZnCl$_4$)$_2$Cl.4H$_2$O to Δ,Λ diol gave a yield of 30 %. Base hydrolysis for 2 min of Δ,Λ-[(en)$_2$Cr(form)-(OH)Cr(en)$_2$](ZnCl$_4$)$_2$ gave similarly Δ,Λ diol in 25 % yield.

REFERENCES

1. Scott, K. L. and Sykes, A. G. *J. Chem. Soc. Dalton Trans.* (1972) 2364.
2. Werner, A. *Justus Liebigs Ann. Chem. 375* (1910) 1.
3. Siebert, H. and Tremmel, G. *Z. Anorg. Allg. Chem. 390* (1972) 292.
4. Wieghardt, K. *J. Chem. Soc. Dalton Trans.* (1973) 2548.
5. Springborg, J. *Acta Chem. Scand. A 32* (1978) 231.
6. Finholt, J. E., Caulton, K., Kimball, K. and Uhlenhopp, E. *Inorg. Chem. 7* (1968) 610.
7. Indubala, S. and Ramaswamy, D. *J. Inorg. Nucl. Chem. 35* (1973) 2055.
8. Springborg, J. and Toftlund, H. *Acta Chem. Scand. A 30* (1976) 171.
9. Toftlund, H. and Springborg, J. *J. Chem. Soc. Chem. Commun.* (1976) 1017.
10. Erdmann, H. *Leder 14* (1963) 249.
11. Erdmann, H. *Leder 17* (1966) 10.
12. Ellis, M. J. and Sykes, R. L. *J. Am. Leather Chem. Assoc. 58* (1963) 346.
13. Ellis, M. J., Shuttleworth, S. G. and Sykes, R. L. *J. Am. Leather Chem. Assoc. 58* (1963) 358.
14. Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*, North-Holland, London 1971, p. 347.
15. Nakamoto, K., Fujita, J., Tanaka, S. and Kobayashi, M. *J. Am. Chem. Soc. 79* (1957) 4904.
16. Mahler, H. R. and Cordes, E. H. *Biological Chemistry*, Harper, New York 1967, p. 194.
17. Bjerrum, J., Schwarzenbach, G. and Sillén, L. G. *Stability Constants of Metal-Ion Complexes*, Part I. The Chemical Society, 1st Ed., London 1957, 2nd Ed., London 1964, 3rd Ed., London 1971.
18. Holwerda, R., Deutsch, E. and Taube, H. *Inorg. Chem. 11* (1972) 1965.
19. Springborg, J. and Schäffer, C. E. *Inorg. Synth. 18* (1978) 75.