Synthesis and Properties of $\mu$-Carboxylato-\textit{O,O}-\mu$-hydroxobis[bis(ethylenediamine)chromium(III)] Salts with Acetate, Formate and Glycinate as Bridging Groups

JOHAN SPRINGBORG$^a$ and HANS TOFTLUND$^b$

$^a$ Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Copenhagen V, Denmark and $^b$ Department of Chemistry, University of Odense, DK-5230 Odense, Denmark

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

Reaction of meso diol, $\Delta\Lambda$-[\(\text{en}\),\(\text{Cr(OH)}_2\)\(\text{Cr(en)}_2\)]\(^{4+}\), with carboxylic acids gives carboxylato-
\(O,O\) bridged complexes of the type $\Delta\Delta$-[\(\text{en}\),\(\text{Cr(RCOO)(OH)}\)\(\text{Cr(en)}_2\)]\(^{4+}\) and crystalline salts have been isolated for $R=\text{CH}_3^-$, $\text{H}^-$, $\text{H}_3\text{NCH}_2^-$ and $\text{H}_2\text{NCH}_2^-$. Salts of the racemic compounds, $\Delta\Delta$ and $\Lambda\Lambda$-[\(\text{en}\),\(\text{Cr(RCOO)(OH)}\)\(\text{Cr(en)}_2\)]\(^{4+}\), 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 (pK$\text{a} \approx 12$), giving blue $\mu$-carboxylato-$\mu$-oxo complexes. The acid dissociation constants, K$\text{a}$, of the ammonium group in the glycinate complexes were determined by glass electrode measurements (pK$\text{a} = 7.5$ for both isomers, 1 M NaClO$_4$, 20 °C).

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

Several binuclear cobalt(III) complexes with carboxylate bridging groups have been described in literature and among the most studied complexes are [(\(\text{NH}_3\))$_4$\(\text{Co(RCOO)(NH}_2\text{Co(NH}_3\text{)}_4\)]\(^{4+}\) and [(\(\text{NH}_3\))$_3$\(\text{Co(RCOO)(OH)}_2\text{Co(NH}_3\text{)}_3\)]\(^{3+}\), 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 ($\Delta\Lambda$) and the racemic ($\Delta\Delta$ and $\Lambda\Lambda$) ethylenediamine diols, [(\(\text{en}\),\(\text{Cr(OH)}_2\)\(\text{Cr(en)}_2\)]\(^{4+}\), rapidly attain equilibrium with their corresponding monoools, [(\(\text{H}_2\text{O}\)\(\text{en}\),\(\text{Cr(OH)}_2\)\(\text{Cr(en)}_2\)]\(^{4+}\), which have been isolated as salts.$^8$-$^9$ For both isomers cleavage of the hydroxo bridge of the monoools 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, $\Delta\Lambda$-[\(\text{en}\),\(\text{Cr(OH)(SO}_4\text{)}\)\(\text{Cr(en)}_2\)]\(^{3+}\)$^5$

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.\textsuperscript{10}–\textsuperscript{13}

The following ligand abbreviations have been used, ac = acetate, form = formate, gly = glycinate = aminoacetate = $H_2NCH_2COO^-$, glyH = ammonioacetate = $H_2NCH_2COO^-$, 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 monols 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 \textit{meso} diol perchlorate, $\Delta,\Lambda$-[(en)$_2$Cr(OH)$_2$-Cr(en)$_2$]ClO$_4$$_n$, was dissolved in 4 M acetic acid at room temperature, the colour of the solution changed within some hours from reddish-purple to red due to the formation of a \textit{\mu}-acetato-\textit{\mu}-hydroxo complex. The complex was isolated as the tetrachlorozincate, $\Delta,\Lambda$-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$]- (ZnCl$_4$)$_2$H$_2$O. The tetrachlorozincate was readily and in high yield converted to the perchlorate dihydrate. Similarly, reaction of \textit{meso} diol perchlorate in 2 M formic acid gave a \textit{\mu}-formato-\textit{\mu}-hydroxo complex isolated as the tetrachlorozincate, $\Delta,\Lambda$-[(en)$_2$Cr(form)(OH)Cr(en)$_2$]ClO$_4$$_n$. This salt was readily converted to the perchlorate. The glycine carboxylato-$O,O$ bridged complex was made by reacting \textit{meso} diol chloride with 2 M glycinium chloride in 0.5 M hydrochloric acid at 55 °C. At this temperature the reaction is rapid ($t_\text{rxn} \approx 10$ min) and $\Delta,\Lambda$-[(en)$_2$Cr(glyH)(OH)Cr(en)$_2$]ZnCl$_4$Cl$\cdot$4H$_2$O could be isolated. In this salt the nonligating amino group in glycine is protonated. From this protonated form the corresponding deprotonated complex was, after removal of zinc as Zn(OH)$_2$, isolated as the red bromide, $\Delta,\Lambda$-[(en)$_2$Cr(gly)(OH)-Cr(en)$_2$]Br$_4$H$_2$O.

The \textit{racemic} carboxylato-$O,O$ bridged complexes were synthesized by methods similar to those described above for the \textit{meso} complexes. Some modifications have been made and these are essentially dictated by difference in solubilities. Generally the \textit{racemic} salts are much more soluble than the corresponding \textit{meso} salts. Furthermore, \textit{racemic} monool, $\Delta,\Delta$- and $\Delta,\Lambda$-[(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 \textit{racemic} complexes.

The \textit{racemic} acetato and formato bridged complexes were both isolated as tetrachlorozincates, $\Delta,\Delta$- and $\Delta,\Lambda$-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$-H$_2$O and $\Delta,\Delta$- and $\Delta,\Lambda$-[(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 \textit{racemic} glycine carboxylato-$O,O$ bridged complex was isolated as the bromide, $\Delta,\Delta$- and $\Delta,\Lambda$-[(en)$_2$Cr(glyH)(OH)Cr(en)$_2$]Br$_4$H$_2$O. This salt was easily converted to the deprotonated form, isolated as the bromide, $\Delta,\Delta$- and $\Delta,\Lambda$-[(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:

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{R} \\
\end{array}
\]

For each carboxylate bridge the pair of isomers, $\Delta,\Lambda$ and ($\Delta,\Delta$- and $\Lambda,\Lambda$), had very similar properties (visible spectra, infrared spectra and acid-base properties), but X-ray powder diffraction diagrams showed unambiguously that different isomers had been formed, \textit{e.g.}, powder diagrams of the two salts $\Delta,\Delta$-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$H$_2$O and $\Delta,\Delta$- and $\Lambda,\Lambda$-[(en)$_2$Cr(ac)(OH)Cr(en)$_2$](ZnCl$_4$)$_2$H$_2$O were clearly different. The assignments of configuration, $\Delta$ and $\Lambda$, 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 $10^{-9} \leq [H^+] \leq 1$ M. This clearly excluded structures having terminal aqua or hydroxo groups and thereby provided strong evidence for the proposed structures. The $\mu$-acetato and $\mu$-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 $\Delta \Lambda$ and $(\Delta \Lambda$- and $\Lambda \Lambda$) isomers in 0.01 M HCl at 25 °C.

<table>
<thead>
<tr>
<th>Cation</th>
<th>$\Delta \Lambda$ Isomer</th>
<th>$\Delta \Lambda$- and $\Lambda \Lambda$ Isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(e, \lambda)_{\text{max}}$</td>
<td>$(e, \lambda)_{\text{max}}$</td>
</tr>
<tr>
<td>$[\text{en}_2 \text{Cr}(\text{ac})\text{OH} \text{Cr}(\text{en}_2)]^{4+}$</td>
<td>(210, 505)</td>
<td>(98.6, 378)</td>
</tr>
<tr>
<td>$[\text{en}_2 \text{Cr}(\text{form})\text{OH} \text{Cr}(\text{en}_2)]^{4+}$</td>
<td>(202, 504)</td>
<td>(89.7, 376)</td>
</tr>
<tr>
<td>$[\text{en}_2 \text{Cr}(\text{glyH})\text{OH} \text{Cr}(\text{en}_2)]^{5+}$</td>
<td>(206, 504)</td>
<td>(84.3, 374)</td>
</tr>
</tbody>
</table>

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 glycinate 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, has been observed previously for the carboxylato bridged complexes $[\text{(NH}_3)_4 \text{Co(COO)} \text{(NH}_2)_2 \text{Co(NH}_3)_4]^{4+}$ and $[\text{(NH}_3)_2 \text{Co(COO)} \text{(OH)}_2 \text{Co(NH}_3)_3]^{3+}$.

From the data in Table 1 the $\Delta$ value for the carboxylato bridged chromium(III) complexes is calculated as 19.82 Kk. This value is close to the $\Delta$ value determined for the complex $\Delta \Lambda-[\text{(H}_2\text{O)}_2 \text{Cr(OH)} \text{Cr(en)}_2 \text{(H}_2\text{O})]^3+$ ($\Delta = 19.88$ Kk). The result is consistent with the observation that carboxylate and water have nearly the same position in the spectrochemical series.

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 $v_{as}(\text{CO})$ is most sensitive to change in the metal. In the carboxylato bridged binuclear cobalt(III) complexes the frequencies $v_{as}(\text{CO})$ are shifted 20 – 50 cm$^{-1}$ to lower frequency compared to the free carboxylates.

The present binuclear chromium complexes show a similar shift in $v_{as}(\text{CO})$ (21 to 28 cm$^{-1}$). Nakamoto has demonstrated that the separation $\Delta \nu$ between the antisymmetric and symmetric stretching frequencies in carboxylato complexes reflects the type of bonding. It was shown that $\Delta \nu$ 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. The relevant data for acetato and formato complexes studied in this work are also shown in Table 2. It is seen that the $\Delta \nu$ 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 expect a higher value of $\Delta \nu$.

Weighardt has demonstrated a linear correlation between the pKa values of the free carboxylic acids and the frequencies $v_{as}(\text{CO})$ of the corresponding $\mu$-carboxylato-di-$\mu$-hydroxo binuclear cobalt(III) complexes. A similar linear relationship apparently holds for $\mu$-carboxylato-$\mu$-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 glycin.$\Delta \nu$ is possible. These estimates gave the value pKa = 4.28 ± 0.1 ($\Delta \nu = 0.25$ °C) (Fig. 1). Combination of this value with the macroscopic acid dissociation constants for glycin,$^1$ pKα = 2.36 and pKβ = 9.91, therefore yields the microscopic equilibrium constants $K_{\alpha \alpha}$ and $K_{\alpha \beta}$ defined by the equilibria

\[\text{H}_2\text{NCH}_2\text{COOH} \rightleftharpoons K_{a3} \text{H}_2\text{NCH}_2\text{COO}^- + \text{H}^+\]

Hence, the pKa values are obtained as $pK_{a3} = 4.28$. 

Table 2. A comparison of antisymmetrical and symmetrical C – O stretching frequencies (cm⁻¹) and the separation of these bands (Δν).

<table>
<thead>
<tr>
<th>Compound</th>
<th>νₐs(CO)</th>
<th>ν₁(CO)</th>
<th>Δν</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(CH₃COO)</td>
<td>1578</td>
<td>1425</td>
<td>153</td>
<td>15</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Co(NH₃)₅(Ch₃COO)</a>₂</td>
<td>1603</td>
<td>1380</td>
<td>223</td>
<td>1</td>
</tr>
<tr>
<td>[(NH₃)₆Co(CH₃COO)(NH₂)₂Co(NH₃)₄]Cl₄·2H₂O</td>
<td>1530</td>
<td>1410</td>
<td>120</td>
<td>1</td>
</tr>
<tr>
<td>Δ,Λ-[{en₂Cr(CH₃COO)(OH)Cr(en)₂}]Cl₄·2H₂O</td>
<td>1552</td>
<td>1418</td>
<td>134</td>
<td>This work</td>
</tr>
<tr>
<td>(Δ,Δ- and Λ,Λ)-[{en₂Cr(CH₃COO)(OH)Cr(en)₂}]Cl₄·2H₂O</td>
<td>1550</td>
<td>1414</td>
<td>136</td>
<td>This work</td>
</tr>
<tr>
<td>Na(HCOO)</td>
<td>1590</td>
<td>1355</td>
<td>235</td>
<td>1</td>
</tr>
<tr>
<td>[Co(NH₃)₅(HCOO)]Br₂</td>
<td>1640</td>
<td>1345</td>
<td>295</td>
<td>1</td>
</tr>
<tr>
<td>[(NH₃)₆Co(HCOO)(NH₂)₂Co(NH₃)₄]Cl₄·4H₂O</td>
<td>1570</td>
<td>1365</td>
<td>205</td>
<td>1</td>
</tr>
<tr>
<td>Δ,Λ-[{en₂Cr(HCOO)(OH)Cr(en)₂}]Cl₄·4H₂O</td>
<td>1569</td>
<td>1379</td>
<td>190</td>
<td>This work</td>
</tr>
<tr>
<td>(Δ,Δ- and Λ,Λ)-[{en₂Cr(HCOO)(OH)Cr(en)₂}]I₄·2H₂O</td>
<td>1569</td>
<td>1376</td>
<td>193</td>
<td>This work</td>
</tr>
<tr>
<td>Δ,Λ-[{en₂Cr(NH₃CH₂COO)(OH)Cr(en)₂}]ZnCl₂·2Cl₄H₂O</td>
<td>1602</td>
<td>1414</td>
<td>188</td>
<td>This work</td>
</tr>
<tr>
<td>(Δ,Δ- and Λ,Λ)-[{en₂Cr(NH₃CH₂COO)(OH)Cr(en)₂}]Br₃·3H₂O</td>
<td>1598</td>
<td>1413</td>
<td>185</td>
<td>This work</td>
</tr>
<tr>
<td>Δ,Λ-[{en₂Cr(NH₃CH₂COO)(OH)Cr(en)₂}]Br₄·4H₂O</td>
<td>1561</td>
<td>1409</td>
<td>152</td>
<td>This work</td>
</tr>
<tr>
<td>(Δ,Δ- and Λ,Λ)-[{en₂Cr(NH₃CH₂COO)(OH)Cr(en)₂}]Br₄·4H₂O</td>
<td>1559</td>
<td>1403</td>
<td>156</td>
<td>This work</td>
</tr>
</tbody>
</table>

Fig. 1. Plot of νₐs(CO) stretching frequency of the bridging carboxylate groups against pKₐ values of the free carboxylic acids, (A) CH₃COOH (pKₐ 4.76), (B) HCOOH (pKₐ 3.75), (C) H₃NC(CH₂COOH (pKₐ 2.36), 17 (ii), Δ,Λ-μ-carboxylato-μ-hydroxobis[bis(ethylenediamine)chromium(III)] complexes; (iv), (Δ,Δ- and Λ,Λ)-μ-carboxylato-μ-hydroxobis[bis(ethylenediamine)chromium(III)] complexes. Dotted lines: Determination of the microscopic acid dissociation constant, Kₐ₃, of glycine from the values of νₐs(CO) of the aminoacetato bridged complexes for the Δ,Λ isomer (I) and the (Δ,Δ- and Λ,Λ) isomers(II), respectively.

H₃N CH₂ COOH $\xrightarrow{K_{ₐ₃}}$ H₂N CH₂ COOH + H⁺

H₂N CH₂ COOH $\xrightarrow{K_{ₐ₅}}$ H₃N CH₂ COO⁻

We thus obtain the values pKₐ₃ = 7.99 ± 0.1 and Kₐ₅ = 4.3 × 10⁻⁵ (I = 0, 25 °C). These microscopic dissociation constants have never been determined previously, but the proposal 17 that the acid dissociation constant for glycine ethyl ester (pKₐ = 7.75, 0.1 M NaNO₃, 25 °C) 17 can be taken as a good estimate of the magnitude of Kₐ₅ is seen to agree with the present data.

Protolytic properties of the complexes. The acid dissociation constants, Kₐ₅, of the glycinoato bridged complexes were determined potentiometrically in 1.0 M NaClO₄ (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 [\{en₂Cr(glyH)(OH)Cr(en)₂\}]⁺ and [\{en₂Cr(glyH)(OH)Cr(en)₂\}]³⁺ in 1.0 M NaClO₄ 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 \( \Delta \lambda \) and \( (\Delta \lambda - \Delta \lambda) \) 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 \([\text{Co}((\text{NH}_{3})_2\text{O})\text{O}CO\text{CH}_2\text{NH}_3]^3+ \) \( (pK_a = 8.5, I = 0.03 \text{ M, } 25 ^\circ \text{C}) \).\(^{18} \)

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 \( \mu \)-carboxylato-\( \mu \)-oxo cations \( (pK_a \approx 12) \). Similar acid properties have recently been reported for the ammonia diol,\(^{19} \) \([\text{NH}_3]_2\text{Cr(OH)}_2\text{Cr(NH}_3)_2]^4+ \), the \textit{meso} and \textit{racemic} isomers of the ethylenediammine diol,\(^{8,9} \) \([\text{en}]_2\text{Cr(OH)}_2\text{Cr(en)}_2]^4+ \), and for the sulfato bridged complex, \( \Delta,\Delta-[\text{en}]_2\text{Cr(OH)(SO}_4)\text{Cr}(\text{en})_2]^3+ \). In all these compounds the hydroxo bridge forms have \( pK_a \approx 12 \) and the oxo bridged forms are blue.

\textbf{Kinetic data.} The reactions between \textit{meso} or \textit{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 \textit{meso} diol in 4 M CH\(_3\)COOH, 4 M HCOOH and 4 M Cl\(^-\), H\(_2\)NCH\(_2\)COOH, respectively, were \( (5 \pm 1) \times 10^{-4} \text{ s}^{-1}, (7 \pm 0.3) \times 10^{-4} \text{ s}^{-1} \), and \( (8 \pm 3) \times 10^{-5} \text{ s}^{-1} \). The rate constants for the reactions of the \textit{racemic} diol were, within experimental error, identical to the respective values for the \textit{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, \( [(\text{H}_2\text{O})\text{en}]_2\text{Cr(OH)}\text{Cr(en)}_2(\text{OOCR})]^4+ \), is also likely to be involved.

\textbf{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 \( \Delta,\Delta \) isomers. In 1 M NaOH the blue \( \mu \)-carboxylato-\( \mu \)-oxo ions, discussed above, decompose giving reddish-purple products. The hydrolysis at 25 \(^\circ \text{C} \) is fairly rapid for the acetato and glycinoato complexes \( (t_1 \approx 5 \text{ min}) \) and very fast for the formato complex \( (t_1 \approx 1 \text{ s}) \). A major part of the hydrolysis process was shown to be carboxylato bridge cleavage giving monool, \( \Delta,\Delta-[\text{OH}(\text{en})_2\text{Cr(OH)(OH)}\text{Cr(en)}_2(\text{OH})]^3+ \). Thus, by acidifying the product solutions it was possible to isolate re-formed \textit{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 \( (t_1 \approx 10 \text{ h}) \) than the formato and glycinoato complexes \( (t_1 \approx 1 \text{ h}) \), as indicated by spectrophotometric measurements at 25 \(^\circ \text{C} \) \( (1 \text{ M NH}_2\text{Cl}, 0.1 \text{ M NH}_3) \). 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.

\section*{EXPERIMENTAL}

\textbf{Materials.} \( \Delta,\Delta-[\text{en}]_2\text{Cr(OH)}_2\text{Cr(en)}_2]^{2+} \) \( (\text{ClO}_4)_4 \), \( \Delta,\Delta-[\text{en}]_2\text{Cr(OH)}_2\text{Cr(en)}_2]^{2+} \) \( (\text{Cl}, 2\text{H}_2\text{O}) \) and \( \Delta,\Delta- \) and \( \Delta,\Delta-[\text{H}_2\text{O}(\text{en})_2\text{Cr(OH)}\text{Cr(en)}_2(\text{OH})]^{3+} \) \( \text{Br}_2, \text{H}_2\text{O} \) were prepared as described in literature.\(^{19,9} \) All other materials were of analytical grade.

\textbf{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.

\textbf{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 \( e \) has been given in \( 1 \text{ mol}^{-1} \text{ cm}^{-1} \) and the wavelength \( \lambda \) 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 CuK\( \alpha \) radiation.

Preparations. 1. \( \Delta\Lambda-\mu-\text{Acetato-\mu-hydroxybis[bis-(ethylenediameine)chromium(III)]} \) tetrachlorozincate. \( \Delta\Lambda-\{[en]_2\text{Cr(ac)OH})\text{Cr}(en)_2\}_2[ZnCl_4]_2 \cdot H_2O \). A solution of \( \Delta\Lambda-\{[en]_2\text{Cr(OH})\text{Cr}(en)_2\} _2\cdot (\text{ClO}_4)_2 \cdot 10 \text{ g, } 12.9 \text{ mmol} \) 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 \( Li_2ZnCl_4 \) (25 ml) gave precipitation of nice red crystals of \( \Delta\Lambda-\{[en]_2\text{Cr(ac)OH})\text{Cr}(en)_2\}_2[ZnCl_4]_2 \cdot H_2O \). 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 \( Li_2ZnCl_4 \) (10 ml) was added to the filtered solution. The precipitate was isolated as above. Yield 4.0 g (100 %). This product was pure. Anal. [\( Cr_2(C_2H_3N_2)_2\cdot (OH)(C_2H_3O_2)_2 \)]\( [ZnCl_4]_2 \cdot H_2O \) (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. [\( Cr_2(C_2H_3N_2)_2\cdot (OH)(C_2H_3O_2)_2 \)]\( [ZnCl_4]_2 \cdot 2H_2O \) (100, 378); (\( e\lambda \) )\( max = (212, 506) \) (500, 555); (\( e\lambda \) )\( min = (43.8, 431) \); medium: 0.01 M HCl; (\( e\lambda \) )\( max = (209, 505) \) (98.6, 377); (\( e\lambda \) )\( min = (44.0, 431) \); medium: 0.1 M ammonium, 0.1 M ammonium chloride; (\( e\lambda \) )\( max = (206, 506) \) (99.6, 376); (\( e\lambda \) )\( min = (45.0, 431) \).

3. \( \Delta\Lambda-\mu-\text{Acetato-\mu-hydroxybis[ethylenedia- mine]chromium(III)} \) tetrachlorozincate. \( \Delta\Lambda-\mu-\{[en]_2\text{Cr(ac)OH})\text{Cr}(en)_2\}_2[ZnCl_4]_2 \cdot H_2O \). Pure \( \Delta\Lambda-\mu-\{[en]_2\text{Cr(OH})\text{Cr}(en)_2\} _2\cdot (\text{ClO}_4)_2 \cdot 10 \text{ g, } 4.09 \text{ mmol} \) 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 aquahydroxy monoonol (which otherwise dissolves slowly in 4 M acetic acid) and a partial precipitation of the bromide salt. The suspension was stirred at 20 °C for 18 h during which time the precipitate dissolved. 4 M \( Li_2ZnCl_4 \) (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 \( Li_2ZnCl_4 \) (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. [\( Cr_2(C_2H_3N_2)_2\cdot (OH)(C_2H_3O_2)_2 \)]\( [ZnCl_4]_2 \cdot H_2O \) (Cr: C, N, H, Cl. Spectral data in 0.01 M hydrochloric acid; (\( e\lambda \) )\( max = (202, 505) \) (96.7, 378); (\( e\lambda \) )\( min = (42.8, 340) \).

4. \( \Delta\Lambda-\mu-\text{Acetato-\mu-hydroxybis[ethylenediamine]chromium(III)} \) iodide. \( \Delta\Lambda-\mu-\{[en]_2\text{Cr(ac)OH})\text{Cr}(en)_2\}_2[I]_2 \cdot H_2O \). Pure \( \Delta\Lambda-\mu-\{[en]_2\text{Cr(ac)OH})\text{Cr}(en)_2\}_2[ZnCl_4]_2 \cdot H_2O \) (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 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. [\( Cr_2(C_2H_3N_2)_2\cdot (OH)(C_2H_3O_2)_2 \)]\( [I]_2 \cdot H_2O \) (Cr: C, H, N, Cl. Spectral data; medium: 0.01 M hydrochloric acid; (\( e\lambda \) )\( max = (203, 505) \) (98.1, 377); (\( e\lambda \) )\( min = (42.3, 430) \); medium 0.1 M ammonium, 0.9 ammonium chloride; (\( e\lambda \) )\( max = (197, 505) \) (94.8, 377); (\( e\lambda \) )\( min = (42.3, 430) \).

5. \( \Delta\Lambda-\mu-\text{Formato-\mu-hydroxybis[ethylenediamine]chromium(III)} \) tetrachlorozincate. \( \Delta\Lambda-\mu-\{[en]_2\text{Cr(form)OH})\text{Cr}(en)_2\}_2[ZnCl_4]_2 \). A solution of \( \Delta\Lambda-\{[en]_2\text{Cr(OH})\text{Cr}(en)_2\} _2\cdot (\text{ClO}_4)_2 \cdot 5 \text{ g, } 6.45 \text{ mmol} \) 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 \( Li_2ZnCl_4 \) (10 ml) was then added. Nice red crystals of \( \Delta\Lambda-\{[en]_2\text{Cr(form)OH})\text{Cr}(en)_2\}_2[ZnCl_4]_2 \) 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 \( Li_2ZnCl_4 \) (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. [\( Cr_2(C_2H_3N_2)_2\cdot (OH)(\text{ClO}_4)_2 \)]\( [ZnCl_4]_2 \cdot Cr: C, N, H, Cl. Spectral data in 0.01 M hydrochloric acid; (\( e\lambda \) )\( max = (200, 504) \) (88.6, 376); (\( e\lambda \) )\( min = (47.5, 431) \).

6. \( \Delta\Lambda-\mu-\text{Formato-\mu-hydroxybis[ethylenedi- amine]chromium(III)} \) perchlorate. \( \Delta\Lambda-\{[en]_2\text{Cr(form)OH})\text{Cr}(en)_2\}_2[\text{ClO}_4]_2 \). Pure \( \Delta\Lambda-\{[en]_2\text{Cr((OH})\text{Cr}(en)_2\}_2[\text{ClO}_4]_2 \cdot 5 \text{ g, } 6.45 \text{ mmol} \) 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. [Cr₂(C₂H₂N₂)₆(ONH)₂(OH)₂]ClO₄·H₂O: Cr, C, H, N, Cl. Spectral data; medium: 1.0 M hydrochloric acid: (ε,λ)max = (202, 505), (92.0, 375.5); (ε,λ)min = (47.8, 431); medium: 0.01 M hydrochloric acid: (ε,λ)max = (204.5, 505), (91.0, 376.5); (ε,λ)min = (48.4, 431); medium = 0.1 M ammonia, 0.1 M ammonium chloride: (ε,λ)max = (195, 505), (94.0, 375); (ε,λ)min = (49.6, 431).

7. (Δ,Δ- and Δ,Λ)-μ-Formato-μ-hydroxobis[bis(ethylene diamine) chromium(III)] tetrachlorozincate. Δ,Δ- and Δ,Λ-[en]₂Cr₄(ONH)₄[Cr(ONH)₂]₂(ZnCl₄)₂. Pure (Δ,Δ- and Δ,Λ)-[en]₂Cr₄(ONH)₄[Cr(ONH)₂]₂(ZnCl₄)₂. Cr₄(ONH)₄[Cr(ONH)₂]₂(ZnCl₄)₂. Cr, C, H, N, Cl. Spectral data in 0.01 M hydrochloric acid: (ε,λ)max = (193, 504), (87.9, 376); (ε,λ)min = (43.8, 430).

8. (Δ,Δ- and Δ,Λ)-μ-Formato-μ-hydroxobis[(ethylene diamine) chromium(III)] iodide. Δ,Δ- and Δ,Λ-[en]₂Cr₄(ONH)₄[Cr(ONH)₂]₂I₂. H₂O. This salt was prepared in the same way as the Δ,Δ- and Δ,Δ-μ-aceto iodide salt, preparation No. 4. Yield: 1.7 g (75 %). Anal. [Cr₂(C₂H₂N₂)₆(ONH)₂(OH)₂]ClO₄·H₂O: Cr, C, H, N, I. Spectral data; medium: 0.01 M hydrochloric acid: (ε,λ)max = (190, 504), (88.4, 376); (ε,λ)min = (45.9, 430); medium: 0.1 M ammonia, 0.9 M ammonium chloride: (ε,λ)max = (196, 504), (86.7, 376); (ε,λ)min = (44.0, 430).

9. Δ,Λ-μ-Ammonioacetato-μ-hydroxobis[(ethylene diamine) chromium(III)] tetrachlorozincate. Δ,Λ-[en]₂Cr₄(ONH)₄[Cr(ONH)₂]₂(ZnCl₄)₂Cl₄H₂O. To a solution of glymine (1.13 g, 15 mmol) in 1 M hydrochloric acid (25 ml) at 55 °C was added Δ,Λ-[en]₂Cr₄(ONH)₄[Cr(ONH)₂]₂Cl₄H₂O (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 Li₂ZnCl₄ (12 ml) was added slowly to the cold solution. Red crystals of the glycinate 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 Li₂ZnCl₄ (5 ml) was added slowly. The precipitate was isolated as above. Yield 1.62 g (81 %). This product was pure. Anal. [Cr₂(C₂H₂N₂)₆(ONH)₂(OH)₂]Cl₄H₂O: C, N, H, Cl. Spectral data; medium: 1.0 M hydrochloric acid: (ε,λ)max = (209, 504), (85.6, 375); (ε,λ)min = (54.2, 431). Medium: 0.01 M hydrochloric acid: (ε,λ)max = (206, 504.5), (84.3, 374); (ε,λ)min = (53.3, 431). Medium: 0.1 M ammonia, 0.1 M ammonium chloride: (ε,λ)max = (206, 505.2), (98.4, 375.5); (ε,λ)min = (41.2, 431).

10. Δ,Λ-μ-Aminoacetato-μ-hydroxobis[(ethylene diamine) chromium(III)] bromide. Δ,Λ-[en]₂Cr₄(glyH)₄[Cr(ONH)₂]₂Br₄·4H₂O. Pure Δ,Λ-[en]₂Cr₄(glyH)₄[Cr(ONH)₂]₂(ZnCl₄)₂Cl₄H₂O (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 (83.3 %) of a pure product. Anal. [Cr₂(C₂H₂N₂)₆(ONH)₂(OH)₂]Br₄·4H₂O: C, N, H, Br. Spectral data in 0.01 M hydrochloric acid: (ε,λ)max = (206, 505), (84.2, 374); (ε,λ)min = (53.8, 431).

11. Δ,Λ-μ-Aminoacetato-μ-hydroxobis[(ethylene diamine) chromium(III)] bromide. Δ,Λ-[en]₂Cr₄(glyH)₄[Cr(ONH)₂]₂Br₄·3H₂O. Pure Δ,Λ- and Δ,Λ-[en]₂Cr₄(glyH)₄[Cr(ONH)₂]₂(ZnCl₄)₂Cl₄H₂O (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 hydrochloric 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 recrystallized from water. Anal. [Cr₂(C₂H₂N₂)₆(ONH)₂(OH)₂]Br₃·3H₂O: C, H, N, Br.

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

12. (Δ,Δ- and Δ,Δ)-μ-Aminoacetato-μ-hydroxobi-
[bis(ethylene diamine) dichromium(III)] bromide. Δ,Δ- and Δ,Δ-μ-[en]_{2}Cr(gly)OHCr(en)_{2}]Br_{4}4H_{2}O. Pure (Δ,Δ- and Δ,Δ)-μ-[en]_{2}Cr(glyH)(OH)Cr(en)_{2}]Br_{3}-
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) were 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})(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; (€λ)_{max} = 192, 505, (82.4, 375); (€λ)_{min} = 50.5, 431.

Powder diagrams. Guinier X-ray powder diagrams of the Δ,Δ isomers of [μ-[en]_{2}Cr(ac)(OH)Cr(en)]_{2}]-
(ZnCl)_{2}4H_{2}O, [μ-[en]_{2}Cr(form)(OH)Cr(en)]_{2}(ZnCl)_{2}4H_{2}O and [μ-[en]_{2}Cr(gly)(OH)Cr(en)]_{2}]Br_{4}4H_{2}O were clearly different from those of their respective (Δ,Δ- and Δ,Δ) isomers.

Potentiometric determination of the acid dissociation constants of the glycine complexes. Solutions of Δ,Δ-μ-[μ-[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 Δ,Δ-μ-[μ-[en]_{2}Cr(OH)(glyH)Cr(en)]_{2}]Br_{4}-
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 ≡ log[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 ≈ 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 [μ-[en]_{2}Cr(gly)(OH)-
Cr(en)]_{2}]Br_{4}4H_{2}O were isolated directly from the basic solutions. Deuterated Δ,Δ-μ-[μ-[en]_{2}Cr(glyH)-
(OH)Cr(en)]_{2}]ZnCl)_{2}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 absorbance in the region 650–350 nm of 3 × 10^{-3} M solutions of meso diol perchorlate or racemic monool bromide in 4 M RCOOH (R = CH_{3}, H-
and OH, "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(ODI − OD_{2}) vs. time for the wavelengths λ = 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 overall rate constant has therefore been obtained.

Carboxylato bridge cleavage. Conversion of μ-μ-[μ-[en]_{2}Cr(ac)(OH)Cr(en)]_{2}]ZnCl)_{2}H_{2}O to Δ,Δ diol tetrachlorozincate was established via base hydrolysis as follows: Δ,Δ-μ-[μ-[en]_{2}Cr(ac)(OH)Cr(en)]_{2}]-
(ZnCl)_{2}4H_{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,Δ 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,Δ diol by comparing its infrared spectrum with that of an authentic sample. Following the procedure above conversion of Δ,Δ-μ-[μ-[en]_{2}Cr(glyH)(OH)Cr(en)]_{2}]-
(ZnCl)_{2}4H_{2}O to Δ,Δ diol gave a yield of 30%. Base hydrolysis for 2 min of Δ,Δ-μ-[μ-[en]_{2}Cr(form)-
(OH)Cr(en)]_{2}]ZnCl)_{2}4H_{2}O gave similarly Δ,Δ diol in 25% yield.

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