Isomerization of Hydroxo Bridged Chromium(III) Complexes

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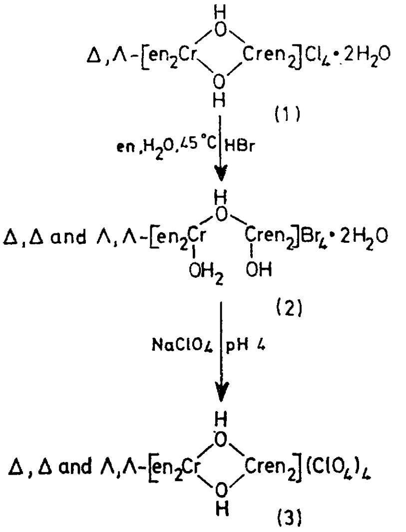
Summary Isomerization of the *meso*-diol $[(en)_2Cr(OH)_2Cr(en)_2]Cl_4.2H_2O$ (**1**) to its *racemic* isomer (**3**) has been achieved, and the new isomers (**2**) and (**3**) have both been isolated as salts.

Hydroxo bridged complexes of bidentate ligands may *a priori* exist as *meso* isomers (Δ,Λ) and as two optically active isomers, (Δ,Δ and Λ,Λ), where the symbols Δ and Λ refer to the chirality of the individual complex units. The two diastereoisomeric forms of $[(en)_2Co(O_2,OH)Co(en)_2](ClO_4)_3{\cdot}H_2O$ (en = ethylenediamine) have been described recently.[1] The synthetic procedures used until now for diols of chromium(III) appear to be stereospecific.[2–5] The isomerization of *meso*- to *racemic*-diol (or *vice versa*) has not been described, either for chromium(III) or, to our knowledge, for any other metal ion. We describe now such an isomerization, as outlined in the Scheme.

The *meso*-diol (**1**) was converted into the *racemic*-mono-ol (**2**) as follows. A solution of (**1**) (0·629 mol/l) in 50% v/v ethylenediamine in water was heated at 45 °C for 1 h. Cooling to 0 °C and slow addition of 65% HBr (1 equiv.) caused precipitation of red crystals of (**2**), yield 64%.

Addition of a large excess of $NaClO_4$ to an aqueous suspension (20 °C, pH *ca.* 4) of (**2**) caused transformation to purple crystals of (**3**), yield 80%, in 30 min.



Scheme

Evidence for the proposed binuclear structure of (**2**) and (**3**) was obtained by comparison with their respective *meso* isomers, the constitution of which is now established.[3,6,7,9] The visible absorption spectra for the two pair of isomers showed great similarities as shown in the Table. In basic solution the cation of (**3**) is deprotonated (pK_a *ca.* 12, 20 °C) to form a blue compound, probably a μ-hydroxo-μ-oxo dimer, as reported for (**1**). Furthermore, (**2**) showed acidic properties in the expected[6,7] region (pK_a 7·7 in 1M $NaClO_4$, 20 °C). The proposed structures of (**2**) and (**3**) were also supported by the very characteristic e.s.r. spectra of these dimers, which at low field are nearly identical to those of their respective *meso* isomers as shown for the diols in the Figure. This great similarity would hardly be found if the skeletons of the bridged cations were different.

Table. Visible absorption spectra at 0 °C in 1 M $NaClO_4$

Cations[a]	λ_{max} (ε)[b]	λ_{max} (ε)
Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$	540 (199)	386 (107)
Δ,Δ- and Λ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$	538 (196)	384 (101)
Δ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+}$	515 (169)	381 (129)
Δ,Δ- and Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+}$	515 (168)	381 (128)

[a] The values for the Δ,Λ isomers are taken from ref. 7. [b] The absorptivities ε are given in l mol⁻¹ cm⁻¹ and the wavelengths λ in nm.

On the other hand (**2**) and (**3**) can unambiguously be distinguished from their respective *meso* isomers by means of *X*-ray powder diffraction patterns (no similarity for salts of the diols with the anions ClO_4^- and Br^- and for the mono-ols with Br^-), i.r. spectroscopy (the bromides of each pair of isomers showed significant differences in the region 1700—300 cm^{-1}), and solubilities (*e.g.* the bromide of the *racemic*-diol is much more soluble than that of the *meso*-diol). In the solid state (**2**) is stable at room temperature for months, while the corresponding *meso* compound is transformed into the *meso*-diol within days. Finally, as described below, the kinetic and thermodynamic parameters for the equilibrium between diol and mono-ol are significantly different for the two systems.

In aqueous solution the cations of (**2**) and (**3**) equilibrate within minutes at room temperature as previously reported[6,7] for the *meso* system. Preliminary values for the equilibration are: $K_{eq} = [(\mathbf{2})]/[(\mathbf{3})] = k_f/k_r = 0{\cdot}2$; $k_f = 1{\cdot}7 \times 10^{-4}\ s^{-1}$; $k_r = 8 \times 10^{-4}\ s^{-1}$, at 0 °C in 1M $NaClO_4$. ($K_{eq} = 0{\cdot}84$; $k_f = 3{\cdot}7 \times 10^{-4}\ s^{-1}$; $k_r = 4{\cdot}2 \times 10^{-4}\ s^{-1}$ for the *meso* system[7]). The kinetics and thermodynamics of this reaction are being studied.

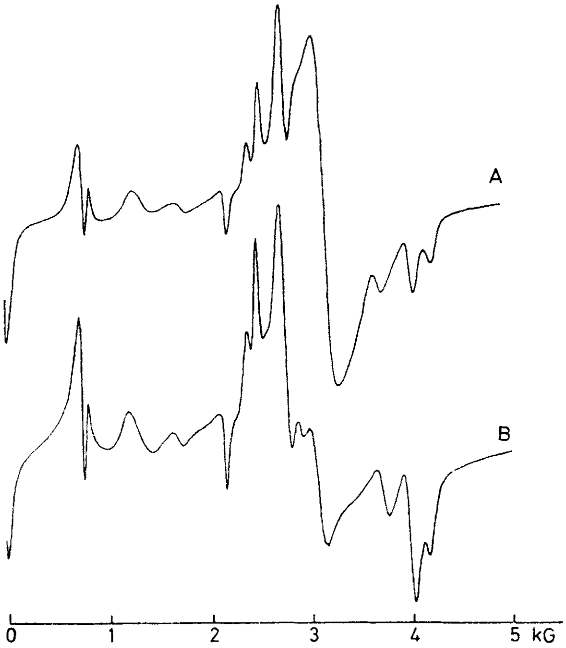


Figure. E.s.r. spectra of the *racemic* (A) and *meso* (B) isomers of $[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$. Solutions (0·01 M in glycerol–10^{-3} M aqueous $HClO_4$, 1 : 1) were made up at 0 °C within 1 min and then frozen to a glass and measurements performed at −140 °C and 9·111 GHz using a JEOL JES-ME-1X spectrometer.

Attempts to achieve equilibrium between the *meso* and *racemic* isomers in aqueous solution were unsuccessful as side-reactions of unknown character predominate within the time-scale of the former reactions; however, starting from the *racemic*-diol bromide a low yield (*ca.* 10%) of the sparingly soluble *meso*-bromide was obtained from an aqueous pyridine buffer solution of (**2**) (pH *ca.* 5, 20 °C, 48 h).

The solid *racemic*-diol bromide quantitatively yielded the *meso*-diol bromide upon heating (30 min, 130 °C). Under similar conditions (**2**) quantitatively yielded the *meso*-diol bromide, probably with the formation of the *racemic*-diol as an intermediate.

As pointed out by Le May and Bailar[8] isomerizations in chromium(III) complexes are not uncommon at elevated temperature. The surprising reaction can be explained as a consequence of a larger lattice energy for the *meso*-bromide salt compared with the *racemic*-bromide salt; this is supported by the fact that the *meso*-diol bromide is much less soluble than the corresponding *racemic*-diol salt.

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[9] The structure of the cation Δ,Λ-$[(OH)(en)_2Cr(OH)Cr(en)_2(OH)]^{3+}$ has now been further established by a single crystal *X*-ray structural analysis of the perchlorate monohydrate salt; K. Kaas, *Acta Cryst.*, submitted for publication.