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Synthesis and Properties of Δ,Λ-μ-Hydroxo-μ-sulfato-bis-[bis(ethylenediamine)chromium(III)] Salts

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The binuclear ion Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$ reacts rapidly with sulfuric acid to give the novel sulfato bridged cation Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2]^{3+}$, isolated as its perchlorate, chloride plus tetrachlorozincate and dithionate salts. The sulfato bridged cation is very robust in the $[H^+]$ region $10^{-7} \leq [H^+] \leq 4$ M. In basic solution it deprotonates ($pK \simeq 12$) giving a blue μ-oxo-μ-sulfato complex which undergoes rapid sulfato bridge cleavage giving the cation Δ,Λ$[(OH)(en)_2Cr(OH)Cr(en)_2(OH)]^{3+}$ as the major product. The oxo bridged cation was isolated as the perchlorate, Δ,Λ-$[(en)_2Cr(O)(SO_4)Cr(en)_2](ClO_4)_2.H_2O$.

Recent studies on the *meso* diol,[1,2] Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$, showed that cleavage of the first bridge by addition of water giving monool, Δ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+}$, occurs several orders of magnitude faster than cleavage of the second bridge. Similar results have recently been obtained for the *racemic* isomers[3] of this diol and of the mixed diol, Δ,Λ-$[(en)_2Cr(OH)_2Co(en)_2]^{4+}$.[4,5] It is now of interest to investigate the reaction of these and of other diols with nucleophiles other than water. The present work describes the novel reaction of *meso* diol with sulfuric acid, and was initiated because of its relevance to the chemistry of chromium tanning.

RESULTS AND DISCUSSION

On dissolution of Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$ in 0.5 M H_2SO_4 (20 °C), the initially purple solution within minutes changes colour giving a wine-red solution from which Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2](ClO_4)_3$ was isolated nearly quantitatively (96 %). From this crude product pure and crystalline salts with the anions perchlorate, chloride plus tetrachlorozincate, and dithionate have been obtained.

The chemical properties of this new dimer provided unambiguous evidence for the proposed structure. The compound reacted neutrally and showed no buffer capacity in the region $1 \leq pH \leq 10$ as indicated by glass-electrode measurements. Furthermore the visible absorption spectrum showed no dependence on $[H^+]$ in the region $10^{-6} \leq [H^+] \leq 4$ M. These results clearly excluded structures having terminal aqua or hydroxo groups, and thereby provided strong evidence for the proposed structure. Other properties mentioned below supported this structure assignment. This assignment has recently been further corroborated by an X-ray structure analysis[6] on the dithionate salt, Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2]_2(S_2O_6)_3.2H_2O$.

The reaction between *meso* diol and sulfuric acid is quantitative and very fast with $k_{obs} = 2.3 \times 10^{-3}$ s^{-1} in 1.0 M sulfuric acid (23 °C). The reaction is therefore unusually rapid as compared to most other reactions involving substitution at a Cr(III) center. This is, however, not surprising as the reaction between *meso* diol and water giving monool similarly has been found to be very rapid.[1] A detailed kinetic study of the reaction between *meso* diol and sulfuric acid is now in progress.

This new dimer is robust in acid and neutral solution but as the pH is increased the sulfato bridge is cleaved rather fast as discussed in the following. When strong base is added to an aqueous solution of Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2](ClO_4)_3$, the colour instantaneously changes from red to blue. The reaction is reversible and is probably due to deprotonation of the acid hydroxo bridge ($pK \simeq 12$, 20 °C, water) giving the blue μ-oxo-μ-sulfato cation. This cation was isolated as its perchlorate, Δ,Λ-$[(en)_2Cr(O)(SO_4)Cr(en)_2](ClO_4)_2.H_2O$. Similar acid properties of the hydroxo bridge have recently been observed for both *meso* and *racemic* isomers of the ethylenediamine diol.[1,3] The μ-oxo-μ-sulfato ion is not stable in solution and the blue solution turns reddish-purple within minutes (1 M NaOH, 20 °C) due to sulfato bridge cleavage, giving monool, Δ,Λ-$[(OH)(en)_2Cr(OH)Cr(en)_2(OH)]^{3+}$. Thus, by acidifying the product solution, it was then possible to isolate re-formed *meso* diol as perchlorate (42 %). Products formed by hydroxo bridge cleavage have not been observed.

The results presented here may prove to be relevant to the chemistry involved in the chromium tanning process. The basic chromium(III) sulfate solutions, used as tanning agent, contain a large number of polynuclear chromium(III) complexes, and it is now well-established that both sulfate and hydroxide are important bridging groups.[7-9] One of the more well-established species is $[H_2O)_4Cr(OH)(SO_4)Cr(H_2O)_4]^{3+}$, characterized in solution only.[8,9] Studies on its ethylenediamine analogue described in this paper might therefore contribute to a better understanding of the chemistry of this class of complexes.

EXPERIMENTAL

Materials. Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$ was prepared as described in literature.[10] All other materials were of analytical grade.

Analysis. Cr and Zn analyses were determined by atomic absorption spectrophotometry. C, N, H, Cl, and S analyses were made by the microanalytical laboratory at the H.C. Ørsted Institute, Copenhagen.

Instruments. A Cary Model 117 spectrophotometer was used for spectrophotometric measurements in the visible region. For the spectrophotometric data given below the absorbancy ε has been given in $l\ mol^{-1}\ cm^{-1}$ and the wavelength λ has been given in nm. Infrared spectra of the compounds in potassium bromide discs were recorded on a Perkin-Elmer 459 grating infrared spectrophotometer.

Preparations. 1. Δ,Λ-μ-Hydroxo-μ-sulfato-bis[bis(ethylenediamine)chromium(III)] perchlorate. Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2](ClO_4)_3$. A solution of Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$ (4.00 g, 5.15 mmol) in 0.5 M sulfuric acid (40 ml, 20 mmol) was kept at room temperature with stirring for 1½ h. The colour of the solution changed from violet to red within minutes after its preparation and after approximately 10 min precipitation of red crystals of Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2](ClO_4)_3$ commenced. After 1½ h a saturated solution of sodium perchlorate (40 ml) was added to the suspension and after a further 20 min the precipitate was filtered off. Washing with 96 % ethanol and drying in the air yielded 3.75 g (96 %). The crude product (2.00 g) was dissolved in 0.5 M hydrochloric acid (70 ml) at room temperature and a saturated solution of sodium perchlorate (30 ml) was then added to the filtered solution. The precipitate was isolated as above. Yield 1.76 g. Anal. $[Cr_2(C_2N_2H_8)_4(OH)(SO_4)](ClO_4)_3$: Cr, C, N, H, Cl, S. Spectral data in 1 M sulfuric acid: $(\varepsilon,\lambda)_{max} = (204{,}508)$, $(104{,}382)$; $(\varepsilon,\lambda)_{min} = (46{,}434)$. The salt is sparingly soluble in pure water, but dissolves readily in, *e.g.*, 1 M solution of sulfuric acid, hydrochloric acid or lithium chloride.

2. Δ,Λ-μ-Hydroxo-μ-sulfato-bis[bis(ethylenediamine)chromium(III)] chloride tetrachlorozincate. Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2]ZnCl_4.Cl.4H_2O$. Crude perchlorate (4.00 g, 5.29 mmol) was dissolved in 0.5 M hydrochloric acid (140 ml) and 4 M Li_2ZnCl_4 (20 ml) was then slowly added to the filtered solution with stirring. After 10 min the precipitate was filtered off, washed with 96 % ethanol and dried in the air. Yield 3.50 g (86 %). The crude salt (2.0 g) was dissolved in water (30 ml) at room temperature, and 4 M Li_2ZnCl_4 (5 ml) was then added slowly to the filtered solution. The precipitate was isolated as above. Yield 1.68 g. Anal. $[Cr_2(C_2N_2H_8)_4(OH)(SO_4)]ZnCl_5.4H_2O$: Cr, Zn, C, N, H, Cl, S. Spectral data in water ($pH \simeq 6$): $(\varepsilon,\lambda)_{max} = (205{,}508), (105{,}382)$. $(\varepsilon,\lambda)_{min} = (45{,}434)$; in 1 M sulfuric acid: $(\varepsilon,\lambda)_{max} = (205{,}508), (105{,}382)$; $(\varepsilon,\lambda)_{min} = (45{,}434)$; in 4 M sulfuric acid: $(\varepsilon,\lambda)_{max} = (208{,}508)$, $(105{,}382)$; $(\varepsilon,\lambda)_{min} = (46{,}434)$. For each medium the spectra changed less than 1 % in absorbancies within 30 min at room temperature.

3. Δ,Λ-μ-Hydroxo-μ-sulfato-bis[bis(ethylenediamine)chromium(III)] dithionate. Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2]_2(S_2O_6)_3.2H_2O$. The dithionate salt was obtained nearly quantitatively by dissolution of the tetrachlorozinkate in a saturated solution of sodium dithionate. The following procedure, which gives a lower yield, was found to give crystals of suitable size for an X-ray crystallographic investigation.[6] To an ice-cold solution of Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2]ZnCl_4.Cl.4H_2O$ (0.85 g, 1.10 mmol) in water (120 ml) was added a saturated (20 °C) solution of sodium dithionate (40 ml) and the solution was kept overnight at 0–5 °C. The crystals were washed with 96 % ethanol and dried in the air. Yield 0.42 g (53 %). Anal. $[Cr_2(C_2N_2H_8)_4(OH)(SO_4)]_2(S_2O_6)_3.2H_2O$: Cr, C, N, H, S. Spectral

data in 1 M H_2SO_4: $(\varepsilon,\lambda)_{max}=(200,508)$, $(101,382)$; $(\varepsilon,\lambda)_{min}=(44,434)$. This salt is nearly insoluble in water.

4. Δ,Λ-μ-Oxo-μ-sulfato-bis[bis(ethylenediamine)-chromium(III)] perchlorate. Δ,Λ-$[(en)_2Cr(O)(SO_4)Cr(en)_2](ClO_4)_2.H_2O$. A suspension of Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2](ClO_4)_3$ (2.00 g, 2.65 mmol) in a mixture of 2 M sodium hydroxide (15 ml) and a saturated solution of sodium perchlorate (5 ml) was stirred at room temperature for 10 min. By this the μ-hydroxo-μ-sulfato complex dissolves and simultaneously bluish-green crystals of Δ,Λ-$[(en)_2Cr(O)(SO_4)Cr(en)_2](ClO_4)_2.H_2O$ separate. The product was washed with 96 % ethanol and then with ether and dried in the air. Yield 1.50 g (84 %). Anal. $[Cr_2(C_2N_2H_8)_4(O)(SO_4)](ClO_4)_2.H_2O$: Cr, C, N, H, Cl. The hydroxo bridged complex is re-formed on acidification: To Δ,Λ-$[(en)_2Cr(O)(SO_4)Cr(en)_2](ClO_4)_2.H_2O$ (0.25 g, 0.37 mmol) was added 1 M $HClO_4$ (4 ml) and the suspension was stirred at room temperature for some minutes. The resulting red precipitate was washed with 96 % ethanol and dried in the air. Yield 0.25 g (89 %). The product was identified as Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2](ClO_4)_3$ by its infrared spectrum.

Sulfato bridge cleavage. Conversion of Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2](ClO_4)_3$ to *meso* diol perchlorate was established *via* base hydrolysis as follows: Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2](ClO_4)_3$ (1.75 g, 2.32 mmol) was dissolved in 1.0 M sodium hydroxide (60 ml) by vigorous stirring at 25 °C for 15 min. Initially formed is a blue suspension containing μ-oxo-μ-sulfato dimer partially precipitated as perchlorate. The final reddish-purple solution containing monool, Δ,Λ-$[(OH)(en)_2Cr(OH)Cr(en)_2(OH)]^{3+}$, as a major product was cooled in ice and then acidified to pH ≃ 7 with 6 M perchloric acid. Then solid sodium perchlorate monohydrate (60 g) was added, and the stirred solution was cooled 1 h. During this time, monool was transformed nearly quantitatively into diol which precipitated as perchlorate. The solid was filtered, washed with 96 % ethanol and dried in the air. Yield 0.75 g (42 %). This product was identified as Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$ by comparing its infrared spectrum with that of an authentic[10] sample.

Spectrophotometric measurements. The formation of Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2]^{4+}$ was followed spectrophotometrically in the region 600 – 350 nm at 23 °C. The changes in the spectrum of a 3×10^{-3} M solution of Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$ in 1.0 M sulfuric acid were timed and after 10 min the spectrum remained constant for at least further 20 min. The final spectrum was identical, within experimental error, with the spectrum of Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2](ClO_4)_3$ in 1 M sulfuric acid. First-order plots of log (OD_t-OD_∞) *vs.* time were linear for at least three half-lifes. From the gradients ($k_{obs}/2.303$) values of the rate-constant, k_{obs}, were calculated and gave $k_{obs}=2.3\times10^{-3}$ s^{-1} independently of the wavelength ($\lambda=520$, 510 and 500 nm).

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