

Synthesis and Properties of Di- μ -hydroxo-bis[bis(trimethylenediamine)chromium(III)] Salts

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In previous studies from this laboratory it was shown that the diols $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4]^{4+}$ and $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2]^{4+}$ (en = 1,2-ethanediamine) obtain equilibrium with their respective parent monohydroxo-bridged complexes, and the thermodynamics and kinetics of these equilibria have been studied in detail.¹⁻³ Continuing these studies we are now investigating other Cr(III) diols and wish here to report the synthesis of a trimethylenediamine diol and the results of its hydrolysis in acid solution. (tn = trimethylenediamine = 1,3-propanediamine).

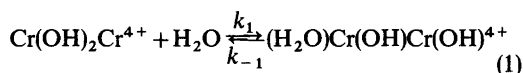
The compound *cis*- $[\text{Cr}(\text{tn})_2(\text{OH})(\text{H}_2\text{O})]\text{S}_2\text{O}_6$ was obtained from *cis*- $[\text{Cr}(\text{tn})_2\text{Cl}_2]\text{Cl}$ via Ag(I) assisted hydrolysis to give, initially, the *cis*-diaqua complex. On heating (140 °C, 45 min), *cis*- $[\text{Cr}(\text{tn})_2(\text{OH})(\text{H}_2\text{O})]\text{S}_2\text{O}_6$ yields the dihydroxo-bridged complex $[(\text{tn})_2(\text{OH})_2(\text{tn})_2](\text{S}_2\text{O}_6)_2$, the diol, nearly quantitatively. This dithionate salt is rather insoluble in water and was therefore converted to the more soluble bromide salt, $[(\text{tn})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{tn})_2]\text{Br}_4 \cdot 2\text{H}_2\text{O}$. The perchlorate salt, $[(\text{tn})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{tn})_2](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$, was obtained from the bromide salt by reprecipitation with sodium perchlorate.

The chemical properties of these salts provide unambiguous evidence for the proposed dihydroxo-bridged structure. The cation gives a neutral reaction and shows no buffer capacity in the region $2 \leq \text{pH} \leq 10$ as determined by glass-electrode measurements. Furthermore, the visible absorption spectrum shows no dependence on $[\text{H}^+]$ in the region $10^{-9} \leq [\text{H}^+] \leq 0.1$ M. These results clearly exclude¹⁻³ structures having terminal hydroxo groups, and when taken in conjunction with the elemental analyses they strongly support the proposed diol structure.

By analogy with its ethylenediamine analogue¹⁻⁶ the cation $[(\text{tn})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{tn})_2]^{4+}$ can exist in two isomeric forms, *viz.* a *meso* (Δ, Δ) and a *racemic* ($\Delta, \Delta - \Lambda, \Lambda$) form. However, the configuration of the present cation has not yet been established.

The spectra of aqueous neutral or acidic solutions of the diol changed with time, but constant

spectra were never obtained. The spectral changes were interpreted on the basis of an initial, relatively fast reaction followed by one or more much slower reactions. Using the method of Guggenheim,⁷ linear plots were obtained for at least three half-lives. Pseudo first-order rate constants, k_{obs} , calculated for the initial fast reaction, gave k_{obs} (25 °C) = $6(1) \times 10^{-4} \text{ s}^{-1}$ in both 0.01 M HClO_4 , 0.09 M NaClO_4 and in 0.1 M NaClO_4 (pH \approx 5). Following our recent results for the corresponding ammonia³ and ethylenediamine^{1,2} systems, we interpret the initial reaction as a bridge-cleavage as shown in eqn. (1) (amine ligands omitted). Therefore $k_{\text{obs}} =$



$k_1 + k_{-1} = 6(1) \times 10^{-4} \text{ s}^{-1}$ is of the same order of magnitude as the value ($5.0 \times 10^{-4} \text{ s}^{-1}$) recently reported³ for the ammonia system.

By analogy with its ammonia and ethylenediamine analogues¹⁻³ the trimethylenediamine diol is a very weak acid ($\text{p}K_{\text{a}} \approx 12$), and it reacts instantaneously and reversibly with hydroxide ions to give a blue complex which is probably a μ -hydroxo- μ -oxo dimer.¹⁻³ The blue oxo-bridged complex reacts in aqueous solution (1 M NaOH, 25 °C) within seconds to give a red solution. No doubt the reaction involves bridge cleavage, but other reactions probably also take place and well-defined products were not isolated.

Experimental. Materials. *cis*- $[\text{Cr}(\text{tn})_2\text{Cl}_2]\text{Cl}$. 0.75 H_2O was prepared as described previously.⁸ All other chemicals were of analytical grade.

Analysis. C, N, H, Cl, and Br analyses were made by the microanalytical laboratory at the H. C. Ørsted Institute, University of Copenhagen.

Spectra. A Zeiss DMR 21 spectrophotometer was used for spectral measurements in the visible region. For the spectral data the absorbancy ϵ is given in $\text{l mol}^{-1} \text{ cm}^{-1}$ and the wavelength λ is given in nm.

Preparations. 1. *cis*-aqua-hydroxobis(trimethylenediamine)chromium(III) dithionate. *cis*- $[\text{Cr}(\text{tn})_2(\text{OH})(\text{H}_2\text{O})]\text{S}_2\text{O}_6$.

A suspension of *cis*- $[\text{Cr}(\text{tn})_2\text{Cl}_2]\text{Cl}$. 0.75 H_2O (3.80 g, 11.9 mmol) and AgNO_3 (6.06 g, 35.7 mmol) in ice-cold 0.001 M HNO_3 (12 ml) was stirred vigorously with cooling in ice for 10 min. Precipitated silver chloride was filtered off and washed with 0.001 M HNO_3 (5 ml). To the combined filtrates was then added, with continued cooling in ice and stirring, a hot (80–90 °C) solution of $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ (3.8 g, 15.7 mmol) in water (10 ml). After further cooling for 10 min pyridine (6 ml) was added dropwise and red crystals of *cis*- $[\text{Cr}(\text{tn})_2(\text{OH})(\text{H}_2\text{O})]\text{S}_2\text{O}_6$ precipitated. The precipitate was

filtered off, washed with 50 % ethanol, then 96 % ethanol and finally with diethyl ether. Drying in the air gave 2.8 g (59 %) of crude *cis*-[Cr(tn)₂(OH)(H₂O)]₂S₂O₆.

2. Di- μ -hydroxo-bis[bis(trimethylenediamine)-chromium(III)] bromide, [(tn)₂Cr(OH)₂Cr(tn)₂]-Br₄·2H₂O.

Solid *cis*-[Cr(tn)₂(OH)(H₂O)]₂S₂O₆ (2.8 g, 7.1 mmol) was heated (140 °C) for 45 min to give 2.4 g of purple diol dithionate. The crude dithionate salt was added to a saturated solution of NH₄Br (30 ml) at room temperature and the suspension was stirred thoroughly for ½ h. The dithionate salt dissolved and reddish-purple crystals of the bromide salt separated. The bromide salt was filtered off, washed with 50 % ethanol, 96 % ethanol and then with diethyl ether. Drying in the air gave 0.95 g of a crude bromide salt. A pure salt was obtained by reprecipitation. The bromide (0.95 g) was dissolved in 0.01 M HBr (30 ml) at room temperature and filtered through a fine porosity sintered glass filter, and then a saturated solution of NH₄Br (30 ml) was added. Crystals of the bromide salt separated within minutes and after 10 min the product was filtered off, washed with 96 % ethanol, ethyl ether and then dried in the air. This gave 0.85 g (30 %) of pure [(tn)₂Cr(OH)₂Cr(tn)₂]-Br₄·2H₂O. The visible absorption spectrum did not change upon further recrystallisation. Anal. [Cr₂(tn)₄(OH)₂]-Br₄·2H₂O: C, H, N, Br. Spectral data at 25 °C: (ϵ, λ)_{max} = (170,533); (89,387). (ϵ, λ)_{min} = (27,6,442); (0.1 M HClO₄). (ϵ, λ)_{max} = (169,533); (89,387). (ϵ, λ)_{min} = (28,0,443). (0.1 M NaClO₄, pH ≈ 5). (ϵ, λ)_{max} = (169,533); (90,387). (ϵ, λ)_{min} = (28,0,443). (0.1 M NH₃, 0.1 M NH₄Cl).

3. Di- μ -hydroxo-bis[bis(trimethylenediamine)-chromium(III)] perchlorate, [(tn)₂Cr(OH)₂Cr(tn)₂]-ClO₄·4·H₂O.

To a solution of diol bromide (0.5 g, 0.63 mmol) in water (10 ml) at room temperature was added a saturated solution of NaClO₄ in water (10 ml). The perchlorate salt precipitated immediately and quantitatively. The precipitate was filtered off and washed with 96 % ethanol and then with diethyl ether. After drying in the air the perchlorate salt was dissolved in water (45 ml), reprecipitated by adding a saturated solution of NaClO₄ in water (8 ml) and then isolated as described above. Yield 0.47 g (88 %). Anal. [Cr₂(tn)₄(OH)₂](ClO₄)₄·H₂O: C, H, N, Cl. The spectral data in water were identical to those given above for the bromide salt. The perchlorate salt is only slightly soluble in perchlorate media and the kinetic measurements have been made in 0.1 M perchlorate media.

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