

**The Chromium Analogue of Werner's Brown Salt: Isolation of
Tris[*cis*-di- μ -hydroxo-bis(ethylenediamine)chromium(III)]-
chromium(III) Nitrate, $[\text{Cr}\{(\text{OH})_2\text{Cr}(\text{en})_2\}_3](\text{NO}_3)_6, \text{aq}$**

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Summary The title compound has been isolated from an aqueous ethylenediamine solution of chromium(III) ions by ion-exchange separation followed by precipitation.

IN connection with investigations of equilibria in aqueous solution between chromium(III) and ethylenediamine (en)¹ we have isolated $[\text{Cr}\{(\text{OH})_2\text{Cr}(\text{en})_2\}_3](\text{NO}_3)_6, \text{aq}$, the chrom-

ium analogue of the tetranuclear cobalt(III) complex often referred to as Werner's brown salt.² It has been isolated from an aqueous solution with the following composition: $[\text{Cr}^{\text{III}}] = 0.03 \text{ M}$, $[(\text{en})\text{H}^+] = 0.4 \text{ M}$, $[(\text{en})\text{H}_2^{2+}] = 0.1 \text{ M}$, and $[\text{Cl}^-] = 1 \text{ M}$ with NaCl. Chromium(III) was added as $[\text{Cr}(\text{en})_3]\text{Cl}_3, \text{aq}$ and the mixture kept at 50 °C for at least 2 days. The chromium species in the resulting mixture

were separated on an ion-exchange column of Sephadex SP-C25. The solution contains mononuclear complexes {mainly *cis*-[Cr(en)₂(OH)₂]⁺} and several polynuclear complexes most of which are purple. These were separated by elution with 0.7M-NaCl, and a red band between two purple bands was concentrated (after dilution × 5) on another column and eluted with 4M-NaClO₄. Hydrolysis (cleavage of the hydroxo-bridges) of this eluate with 12M-HClO₄ gave a mixture of *cis*-[Cr(en)₂(H₂O)₂]³⁺ and [Cr(H₂O)₆]³⁺ as shown by e.s.r. measurements.

We now added solid LiNO₃ and EtOH to a corresponding 4M-LiNO₃ eluate and after a few hours at -20 °C red crystals of [Cr{(OH)₂Cr(en)₂}₃](NO₃)₆.aq precipitated, which could be reprecipitated from 50% EtOH with solid LiNO₃; the crystals were washed with EtOH. We also isolated the iodide by dissolving the nitrate in water, precipitating with NaI, and washing with EtOH.

¹ P. Andersen and T. Berg, to be published.

² A. Werner, *Ber.*, 1907, **40**, 2103.

³ U. Thewalt, *Chem. Ber.*, 1971, **104**, 2657.

Hydrolysis of the nitrate and of the iodide with 9M-HClO₄ saturated with NaClO₄ gave 75 mol-% *cis*-[Cr(en)₂(H₂O)₂]³⁺ and 25 mol-% [Cr(H₂O)₆]³⁺ as shown by e.s.r. measurements directly on frozen glycerol glasses of the hydrolysis mixture, and also by ion-exchange separation of the hydrolysis products.

Cr, N, and I analyses were in agreement with the formulae [Cr{(OH)₂Cr(en)₂}₃](NO₃)₆.aq and [Cr{(OH)₂Cr(en)₂}₃]I₆.aq.

X-Ray powder photographs of the nitrate show that it is isomorphous with the corresponding cobalt(III) salt. A crystal structure analysis of [Co{(OH)₂Co(en)₂}₃](S₂O₈)₃.aq, obtained by metathesis of Werner's corresponding nitrate, shows that the absolute configuration of the three cobalt atoms surrounding a Λ central cobalt atom is Δ , Δ , and Λ .³

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