

Short Communication

Synthesis of *cis*-Tetraammine Chromium(III) Complexes

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There exist good literature methods for the preparation of hexaammine,^{1–3} pentaammine,^{4,5} *trans*-tetraammine,⁶ and *mer*- and *fac*-triammine chromium(III)⁷ complexes. On the other hand, the known methods for the preparation of *cis*-tetraammine chromium(III) complexes give the desired products in rather low yields⁸ or only as minor biproducts.⁶

The formation of chromium(III) ammine complexes in aqueous ammonia solution is hindered due to the presence of hydroxide ions which compete effectively with ammonia as ligands. In order to overcome this difficulty the following two strategies can be used. First, aerial or solvent oxidation of Cr^{II} in ammonium/ammonia buffers leads, depending on the experimental conditions, to the isolation of several products.^{9–11} Secondly, a better way to avoid the competition of hydroxide ions is to work under more or less anhydrous conditions.^{1,6,7}

As relevant examples for both strategies, we can briefly mention the following syntheses. Cr(NH₃)₆³⁺ can be synthesized from anhydrous CrCl₃ and liquid ammonia containing amide,¹ as well as from Cr^{II} in an ammonium/ammonia buffer containing a homogeneous² or an inhomogeneous³ catalyst. These three methods give yields from 70 to 100%. Aerial oxidation of Cr^{II} in an ammonium/ammonia buffer leads to the formation of the acid rhodo ion, [(NH₃)₅Cr(OH)Cr(NH₃)₅]⁵⁺, in 60% yield. Since the hydroxo bridge in this dimeric complex can be cleaved with acid, this compound offers an entrance to the pentaammine series.¹² The reaction of *trans*-[Crpy₄F₂]I (py = pyridine) with liquid ammonia results in a close to quantitative formation of *trans*- and *cis*-[Cr(NH₃)₄F₂]I in the ratio 3:1.⁶ [Crpy₃F₃] reacts quantitatively with liquid ammonia to produce *mer*-[Cr(NH₃)₃F₃], which completely isomerizes to *fac*-[Cr(NH₃)₃(CF₃SO₃)₃] in neat triflic acid (CF₃SO₃H).⁷

In stark contrast to all the abovementioned methods, the best entrance to the *cis*-tetraammine series gives the initial products *cis*-[Cr(NH₃)₄H₂OCl]Cl₂ and *cis*-[Cr(NH₃)₄H₂OCl]SO₄ in yields varying between 25 and 40%.⁸

In connection with numerous, but unsuccessful,¹³ attempts to improve the syntheses of the chromium(III) analog¹¹ of Werner's brown salt, the need for easy and high-yielding preparative methods of *cis*-tetraammine chromium(III) complexes led us to the syntheses described in this preliminary study {in Werner's brown cation [Co{(OH)₂Co(NH₃)₄}]⁶⁺ three *cis*-[Co(NH₃)₄(OH)₂]⁺ ions act as ligands on the central cobalt ion}. The method is inspired by the procedures used in Refs. 6 and 7, and makes use of the fact that oxalato-pyridine complexes of chromium(III) react with liquid ammonia to produce mainly [Cr(NH₃)₄ox]₂ox (ox = oxalate = C₂O₄²⁻).

Experimental and results

Materials. The chemicals used were of reagent grade.

Analysis. The synthesized compounds were analysed on a microscale for Cr, C, H, N, Cl and Br.

Syntheses.

Oxalatotetrakis(pyridine) chromium(III)-bis(oxalato)-bis(pyridine) chromium(III), [Crpy₄ox][Crpy₂ox₂], **1**. Cr(NO₃)₃·9H₂O (200 g, 0.5 mol) was heated to 90–100 °C with oxalic acid dihydrate (H₂C₂O₄·2H₂O, 94 g, 0.75 mol) and 300 ml of water. All the nitrate was reduced by slow addition of formalin (CH₂O, 25% aqueous solution, 60 ml). The resulting solution of chromium(III) oxalate was evaporated to the consistency of porridge and then added to 1.5 l of pyridine. The

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water was then distilled off with the pyridine (pyridine–water azeotrope, 43% water, b.p. 93 °C), whereby a red–violet microcrystalline product formed almost immediately. The distillation continued until the temperature of the leaving vapours reached 115 °C (b.p. of pyridine). After being cooled to room temperature, the crystals were filtered off, washed with acetone and dried on the filter. The crystals crumbled and became non-transparent during the isolation process, probably due to loss of co-crystallized pyridine. Yield: 194 g (92%). Analyses: Found Cr 12.59; C 50.46; H 4.03; N 10.40. Calculated for **1**: Cr 12.35; C 51.31; H 3.59; N 9.97.

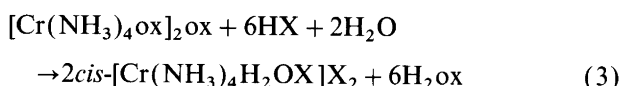
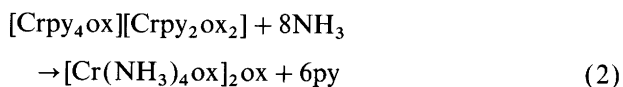
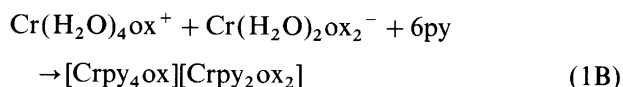
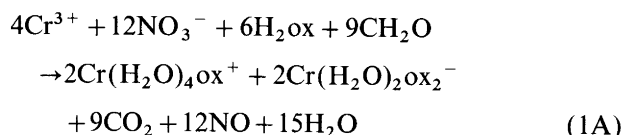
Oxalatotetraamminechromium(III) oxalate, $[\text{Cr}(\text{NH}_3)_4\text{ox}]_2\text{ox}$, **2**. 50 g of **1** and 200 ml of liquid ammonia were allowed to react at 100 °C in a closed steel autoclave (volume 250 ml) for three days. After cooling, the red precipitate was filtered off. The filtrate was colourless. The precipitate was washed with methanol. Yield 30 g of crude **2**. The elemental analyses indicated that this was contaminated by $[\text{Cr}(\text{NH}_3)_4\text{ox}][\text{Cr}(\text{NH}_3)_2\text{ox}_2]$. Analyses: Found Cr 20.90; C 14.48; H 4.63; N 21.37. Calculated for **2**: Cr 20.62; C 14.29; H 4.80; N 22.22. This product was used without further purification in the subsequent reaction.

Aquachlorotetraamminechromium(III) chloride, $[\text{Cr}(\text{NH}_3)_4\text{H}_2\text{OCl}]\text{Cl}_2$, **3**. 10 g of crude **32** were dissolved in 50 ml of concentrated hydrochloric acid. The solution was boiled for 5 min. The red crystals were isolated from the blue–green filtrate by filtration. After being washed with half-concentrated hydrochloric acid and then ethanol, the yield was 7 g (72%) of pure **33**. Analyses: Found Cr 21.41; H 5.85; N 22.13; Cl 43.15. Calculated for **2**: Cr 21.27; H 5.77; N 21.92; Cl 43.50. Pure $[\text{Cr}(\text{NH}_3)_4\text{H}_2\text{OBr}]\text{Br}_2$ was prepared by the same method and in similar yields. Analyses: Found Cr 13.87; H 3.78; N 14.12; Calculated for $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]\text{Br}_2$: Cr 13.76; H 3.73; N 14.83.

Pyridinium[bis(oxalato)bis(pyridine)chromate(III)] hydrate, $\text{pyH}[\text{Crox}_2\text{py}_2] \cdot \text{H}_2\text{O}$, **4**. The crude compound was synthesized as **1**, but with a Cr:ox ratio of 1:2. The yield was quantitative. Soxhlet extraction with pyridine gave analytically pure **4**. Analyses: Found Cr 10.95; C 47.04; H 3.74; N 8.75. Calculated for **4**: Cr 10.73; C 47.12; H 3.74; N 8.68. The analytically pure water-free ammonium salt could be obtained by dissolving **4** (10 g) in water (200 ml) followed by addition of a saturated NH_4Cl solution (20 ml). Yield: 7.8 g of pure $\text{NH}_4[\text{Crox}_2\text{py}_2] \cdot \text{H}_2\text{O}$. Analyses: Found Cr 12.46; C 39.82; H 3.39; N 10.09. Calculated for $(\text{NH}_4)[\text{Crox}_2\text{py}_2] \cdot \text{H}_2\text{O}$: Cr 12.31; C 39.82; H 3.34; N 9.95.

Discussion

All the relevant reactions are collected in Scheme 1. For obvious reasons we tried to improve the stoichiometry of the first reaction (step 1A in Scheme 1) by having a chromium:oxalate:nitrate ratio of 1:1:1. However,



Scheme 1. Overview of the reactions relevant for this study ($\text{X}^- = \text{Cl}^-$, Br^- ; py = pyridine and ox = oxalate).

these attempts only resulted in the formation of **1** accordingly lower yields (step 1B in Scheme 1). Our identification of **1** as $[\text{Crypy}_4\text{ox}][\text{Crypy}_2\text{ox}_2]$ is not unambiguous. It is based on the elemental analysis, on the yield of the synthesis, and on comparison of the solubility properties of **1** with similar double salts. Compound **1** is, as is $[\text{Cr}(\text{oxen}_2)[\text{Crox}_2\text{en}_2] \cdot x\text{H}_2\text{O}$ (en = ethylenediamine),¹⁴ insoluble in all solvents. Of interest in this context is that if we used a chromium:oxalate ratio of 1:2 in step 1A, we isolated in step 1B the pure compound **4**. When **4** rather than **1** was used in the subsequent steps we also isolated *cis*- $[\text{Cr}(\text{NH}_3)_4\text{H}_2\text{OCl}]\text{Cl}_2$, but always in somewhat lower yields (62%).

The identification of **2** as mainly $[\text{Cr}(\text{NH}_3)_4\text{ox}]_2\text{ox}$ is based on the yield, the elemental analyses of the product from the reaction (step 3 in Scheme 1) as well as from the behaviour of this product in the subsequent reaction (step 3 in Scheme 1). The elemental analyses of the crude **2** always indicated a Cr:N ratio somewhat less than 4 (see below).

Reaction step 3 in Scheme 1 is essentially the same as described by Schlessinger.¹⁰ The removal of the coordinated oxalate with acid proceeds with retention of the configuration, i.e. tetraammineoxalatochromium(III) yields *cis*-tetraamminechromium(III) complexes. The blue–green filtrate observed when isolating **3** indicates presence of *cis*-diammine-*trans*-dichlorodiaquachromium(III) ions.¹¹ From this fact we conclude that the crude **2** is contaminated with *cis*- $[\text{Cr}(\text{NH}_3)_2\text{ox}_2]^-$, e.g. $[\text{Cr}(\text{NH}_3)_4\text{ox}][\text{Cr}(\text{NH}_3)_2\text{ox}_2]$. This is in agreement with the elemental analyses of the crude **2** which always gave a Cr:N ratio somewhat less than 4.

In conclusion, we have demonstrated that pyridine–oxalate complexes of chromium(III) are good starting materials for *cis*-tetraamminechromium(III) complexes. The yield in the synthesis of *cis*- $[\text{Cr}(\text{NH}_3)_4\text{H}_2\text{OCl}]\text{Cl}_2$ has been improved by a factor of two compared to previous methods.

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