# 109. A New Route to Crystalline Salts of the Hydrolytic Dimer of Chromium(III)

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Crystalline salts of the hydrolytic dimer of Cr(III), $[Cr_2(\mu\text{-}OH)_2(H_2O)_8]X_4\cdot n\ H_2O$ ($X = p$-toluenesulfonate (tos) or mesitylene-2-sulfonate (dmtos)) have been prepared in good yields *via* a simple two-step procedure: $H^+$ oxidation of Cr metal to give $Cr^{2+}$ ($T \approx 70°$) followed by $O_2$ oxidation, of $Cr^{2+}$ to give the dimer ($T \approx 25°$). The mechanism of conversion of $Cr^{2+}$ into the dimer is discussed.

**Introduction.** – A major objective of work on the hydrolytic polymerization of Cr(III) is the structural characterization of hydrolytic oligomers. The first such structure to be reported, that of the hydrolytic dimer $[Cr_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ [1] confirmed predictions made on the basis of its solution properties [2–4]. The synthetic procedure involved the preparation of the 'active' dimer hydroxide. Dissolution of this hydroxide in a suitable acid led to the crystallization of the dimer. However, difficulties were encountered in the isolation of the finely dispersed 'active' hydroxide, and each preparation afforded only small amounts of hydrolytic dimer salts.

We report here a more convenient synthesis of crystalline dimer salts based on the oxidation of Cr metal to $Cr^{2+}$ in the presence of a suitable aromatic sulfonic acid, followed by oxidation of $Cr^{2+}$ with $O_2$ to generate the dimer.

**Experimental.** – *Materials.* Cr metal (*Balzers*, 99.9%), mesitylene-2-sulfonic acid (*Fluka, purum*), and TsOH (*Unilab*, LR) were all used without further purification.

*Synthesis of* $[Cr_2(\mu\text{-}OH)_2(H_2O)_8][(CH_3)_3C_6H_2SO_3]_4\cdot 4\ H_2O$. Cr metal (1 g, 0.019 mol) was added to 200 ml of $H_2O$ in a three-neck round-bottom flask fitted with a $N_2$ inlet and outlet, thermometer, and magnetic stirrer. The soln. was brought to the desired temp. (60–90°) and deoxygenated by bubbling $N_2$ through it. The $N_2$ flow was stopped, and solid mesitylene-2-sulfonic acid (4.49 g, 0.019 mol) was added directly onto the surface of the metal. After a few seconds, the evolution of $H_2$ and appearance of a sky-blue colour (characteristic of $Cr^{2+}$) was observed indicating that the reaction had commenced. The reaction was allowed to continue, whilst bubbling with $N_2$, until the evolution of $H_2$ ceased (*ca.* 2 h). An excess of Cr metal was used partly to increase the surface area, but more importantly, to avoid a large excess of acid which could lead to dimer cleavage during workup. The soln. was cooled to r.t. and then bubbled with $O_2$, until conversion into the dark blue-green dimer was complete (*ca.* 0.5 h). Occasionally, a light-blue precipitate, presumably $[Cr(H_2O)_6](dmtos)_2$ formed on cooling, but redissolved on bubbling with $O_2$. (Poorer yields were obtained when $O_2$ oxidation was carried out at higher temp., 80–90°.) The resulting dimer soln. was filtered to remove excess Cr metal, reduced in volume to the point where crystal growth became apparent, and then stored at 2°. The dark blue-green crystals that formed overnight were collected and washed with mildly acidic ice-cold $H_2O$ (acidified to pH ~ 2 to suppress polymerization of dimer). Further crops of

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the product were obtained on evaporation of the supernatant. A yield, calculated from the amount of Cr metal consumed, of 3.32 g (74%) was obtained, when Cr metal was oxidised with $H^+$ at 70°. Lower yields were obtained for reaction temp. either side of this (*e.g.* 49% at 60° and 53% at 90°). The composition of the product was identical to that reported in [1].

*Synthesis of* $[Cr_2(\mu\text{-}OH)_2(OH_2)_8]\ (CH_3C_6H_4SO_3)_4 \cdot n\ H_2O$. The procedure was as described above except that $TsOH \cdot H_2O$ (3.66 g, 0.019 mol) was used as the acid. It was found that this acid was not always efficient at initiating reaction with Cr metal. This was overcome by addition of a drop of conc. HCl directly onto the surface of the metal. Analysis of a representative sample indicated the product most likely contains 13 $H_2O$ of crystallization, although this does vary from sample to sample. Typical yield for $H^+$ oxidation at 70° was 4.5 g (80%). Anal. calc. for $C_{28}H_{72}O_{35}S_4Cr_2$: C 28.0, H 6.0, S 10.7, Cr 8.7; found: C 28.0, H 6.1, S 10.8, Cr 8.7.

**Discussion.** – The addition of either mesitylene-2-sulfonic acid or TsOH to Cr metal at temperatures between 60 and 90° results in the formation of sky-blue solutions of $Cr^{2+}$ and concurrent liberation of $H_2$. Further oxidation with $O_2$ generates the hydrolytic dimer $[Cr_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ which could be isolated as either the mesitylene-2-sulfonate or *p*-toluenesulfonate salt. The yield was found to be affected by the temperature of oxidation of both Cr metal and $Cr^{2+}$. Optimum yields were obtained, when oxidation of Cr metal by $H^+$ and of $Cr^{2+}$ by $O_2$ were carried out at 70 and 25°, respectively.

The variation in yield with the temperature of $H^+$ oxidation of Cr metal may be rationalized in the following way:

*i)* At higher temperatures (80–90°), the reaction is vigorous and proceeds to the point where the $[H^+]$ left in the $Cr^{2+}$ solution is quite low ($< 10^{-3}$ M). These conditions favour the polymerization of dimer during oxidation of $Cr^{2+}$ and subsequent workup to obtain the product. This interpretation is strongly supported by the fact the colour of these solutions (dark-green) was no longer that of the dimer (dark-blue).

*ii)* At lower temperatures ($< 70°$), reaction between $H^+$ and Cr metal is sluggish and may stop before completion leaving an excess of acid in solution. This could lead to the acid-induced cleavage of some of the dimer during subsequent treatment.

Thus, a temperature of *ca.* 70° represents the best compromise between these opposing effects and gives the highest yield.

Higher yields were also obtained, when $O_2$ oxidation is carried out at 25° rather than at higher temperatures. This might be expected, since hydrolytic processes (whether cleavage or polymerization) are faster at higher temperatures.

The mechanism of $O_2$ oxidation of $Cr^{2+}$ is of interest especially, because the product differs from that obtained by reaction of $Cr^{2+}$ with one electron oxidants (*e.g.* $Fe^{2+}$, $Cu^{2+}$, and $Cl_2$), where $Cr^{3+}$ is the major or only product [2]. Conversion of $Cr^{2+}$ into the hydrolytic dimer may be envisaged to occur *via* a complex series of relatively rapid reactions (*Eqns. 1–6;* $H_2O$ ligands omitted for clarity).

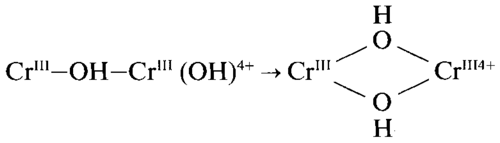
$$Cr^{2+} + O_2 \rightleftharpoons Cr^{II}O_2^{2+} \rightleftharpoons Cr^{III}(O_2^-)^{2+} \tag{1}$$

$$Cr^{III}(O_2^-)^{2+} + Cr^{2+} \rightarrow Cr^{III}{-}O{-}O{-}Cr^{III\,4+} \rightarrow 2Cr^{IV}O^{2+} \tag{2}$$

$$Cr^{IV}O^{2+} + Cr^{2+} \rightarrow Cr^{IV}{-}O{-}Cr^{II\,4+} \rightarrow Cr^{III}{-}O{-}Cr^{III\,4+} \tag{3}$$

$$Cr^{III}{-}O{-}Cr^{III\,4+} \overset{H^+}{\rightleftharpoons} Cr^{III}{-}OH{-}Cr^{III\,5+} \tag{4}$$

$$Cr^{III}{-}OH{-}Cr^{III\,5+} \rightleftharpoons Cr^{III}{-}OH{-}Cr^{III}\,(OH)^{4+} + H^+ \tag{5}$$



(6)

Analogous mechanisms have been proposed for the reaction of $O_2$ with ammoniacal solutions of Cr(II) [5], Cr(II) porphyrins [6], and some divalent complexes of Co [7], V [8], and Fe [9].

The proposed mechanism for $Cr^{2+}$ oxidation *(Eqns. 1–6)* is strongly supported by the following facts *i)* $Cr^{III}(O_2^-)^{2+}$ *(Eqn. 1)* is kinetically stable in acidic solution and has been studied in detail [10] [11]; *ii)* $Cr^{IV}O^{2+}$ porphyrin complexes have been prepared, by reaction of Cr(II) porphyrins with $O_2$ in non-aqueous solvents, and found to give oxo-bridged dimers when reacted with Cr(II) complexes *(Eqn. 3)* [6]; *iii)* $^{18}O$-labelling experiments have shown that the oxidant is incorporated in the bridge [5]; *iv)* Since the reaction is carried out in acidic solution (pH $\sim$ 2), protonation of the oxo-bridged dimer *(Eqn. 4)* is expected, as is observed for $[(NH_3)_5Cr{-}O{-}Cr(NH_3)_5]^{4+}$ at pH $< 7$ [12]; *v)* the pathway for conversion of singly bridged into doubly bridged dimer (*Eqns. 5* and *6*) is well established [13] and has been the subject of recent investigations [14].

In conclusion, this new synthesis of hydrolytic dimer salts is more efficient and adaptable for larger-scale preparation than the previously used method involving the 'active' dimer hydroxide [1]. It is also better suited for the preparation of dimer solutions in perchlorate media than methods based on reduction of $Cr^{3+}$ with Zn amalgam to give $Cr^{2+}$ followed by $O_2$ oxidation to the dimer [15].

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