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PROGRESS IN THE CHEMISTRY OF CHROMIUM(V) DOPING AGENTS
USED IN POLARIZED TARGET MATERIALS

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We wish to report progress in two areas of the chromium(V)-based doping agents:

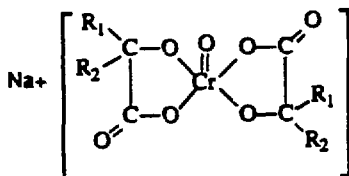
I. Two commonly used chromium(V) complexes, I and II, have been synthesized in perdeuterated form (i.e., all hydrogens replaced by deuterium). They are sodium bis(2-ethyl-2-deuteroxybutyrate)oxochromate(V) monodeuterate, IV, (acronym EDDBA-Cr(V)), and sodium bis(2-deuteroxy-2-methylpropionate)oxochromate(V), III, (acronym DMPA-Cr(V)).

II. A synthetic route leading to the preparation of stable, chromium(III)-free solutions of chromium(V) in diols (1,2-ethanediol /ethylene glycol/ and 1,2-propanediol /propylene glycol/) has been outlined.

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I. Synthesis of Perdeuterated Complexes of Chromium(V)

The role of chromium(V) complexes used as doping agents for the preparation of polarized target materials has met with success. The complexes have been used in a variety of experiments ranging from dynamic polarization of protons¹, deuterons², carbon-13³ and fluorine-19⁴ nuclei to biomolecules^{5,6}. In recent years there has been a growing interest in polarized targets containing only the ²H (deuterium) nucleus in the absence of any protons. For the purpose of these experiments we have decided to synthesize the most often used complex, sodium bis(2-ethyl-2-hydroxybutyrate)-oxochromate(V) monohydrate, II, (common acronym EHBA-Cr(V)) in perdeuterated form. In addition, we have also prepared sodium bis(2-hydroxy-2-methylpropionate)oxochromate(V), I, (acronym HMPA-Cr(V)) in perdeuterated form as its synthesis is less demanding and less costly. It was used in initial test experiments⁷.



- I. R₁, R₂ = CH₃
- II. R₁, R₂ = C₂H₅
- III. R₁, R₂ = CD₃
- IV. R₁, R₂ = C₂D₅

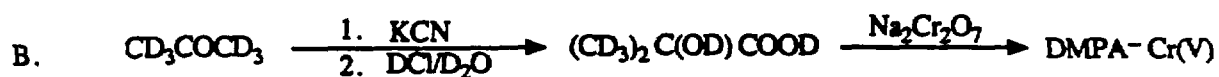
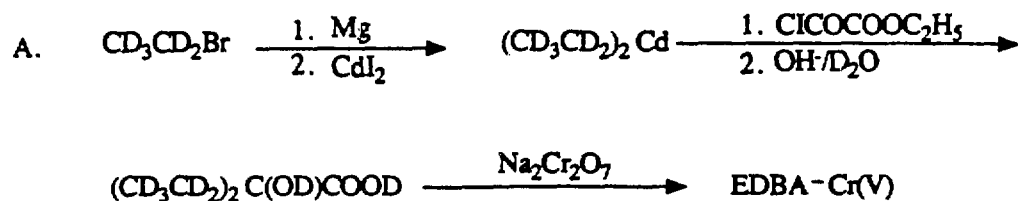
Scheme I outlines individual steps leading to preparation of deuteroxy acids used as starting materials. As both acids are not commercially available they had to be synthesized from simple deuterated molecules. The first complex, EDDBA-Cr(V), IV, was prepared from bromoethane-d₂ via a series of organometallic reactions (Grignard, organocadmium) to give 2-ethyl-2-deuteroxybutyric acid-d₁₂. The synthesis of the second complex, DMPA-Cr(V), III, was relatively fast. Acetone-d₆ was

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converted into a cyanohydrin which after hydrolysis yielded 2-deuteroxy-2-methylpropionic acid-d₄. Both deuteroxy acids were then oxidized to form chromium(V) complexes⁸. Experimental details of this procedure will be published elsewhere⁹.

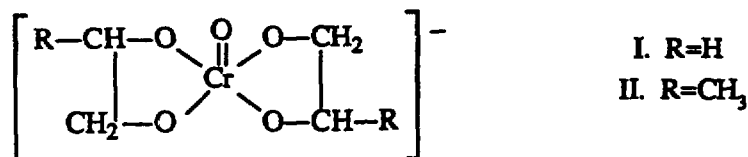
Scheme I



II. Complexes of Chromium(V) with Diols (Glycols)

Before the introduction of externally available chromium(V) complexes chromium(V) in diols was generated in situ.¹⁰ Typically, a procedure described by Bontchev¹¹ was followed using potassium dichromate dissolved in excess ethylene glycol. The oxidation was allowed to proceed for some time in order to accumulate a chromium(V)-ethylene glycol complex, I, along with chromium(III), water and other reaction products. The complex was never isolated in pure form, the solution was used directly to produce polarized targets.

Encouraged by our successful synthesis of chromium(V) complexes based on hydroxy acids⁸ we turned our attention to two diols, 1,2-ethanediol (ethylene glycol) and 1,2-propanediol (propylene glycol), in an attempt to prepare complexes I and II.



First, we have noticed an unusually high reaction photosensitivity (Fig. 1), much higher than previously reported¹¹. The maximum at 600 nm is indicative of the formation of chromium(III)^{12,13}. Thus, all experiments were then performed in the absence of light. Having substantially changed reaction conditions — using a near stoichiometric ratio between the diols and sodium dichromate — we were able to considerably increase the amount of chromium(V) formed. The decomposition of chromium(V) is also accelerated by the presence of water formed in the course of oxidation¹¹. Thus, we used a common dehydrating agent, anhydrous magnesium sulfate, to continuously remove water. These results are summarized in Fig. 2.

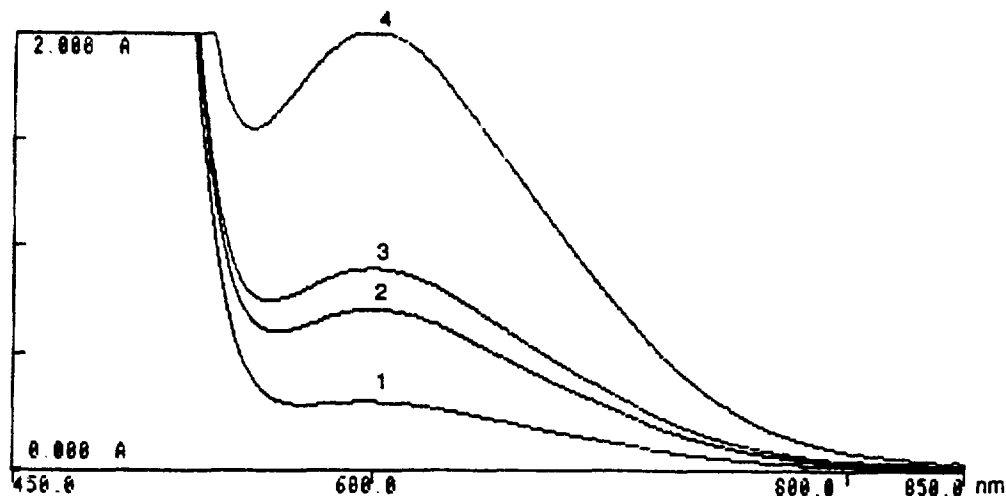


Figure 1. Visible spectrum scans of the initial stage of the oxidation of 1,2-propanediol by sodium dichromate (11:1, w/w, 25° C). Effect of light. Time: (1), 4 hr, dark; (2), 4 hr, incandescent lab light; (3), 10 min, sunlight; (4), 4hr, sunlight.

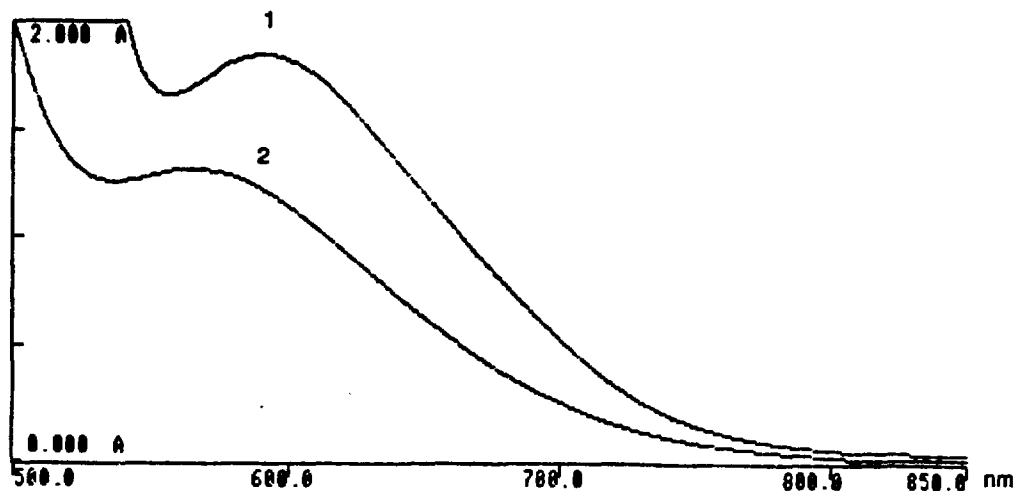


Figure 2. Visible spectrum scans of the initial stage of the oxidation of 1,2-propanediol by sodium dichromate (stoichiometry 1.2: 1 mol; 25° C). Effect of water. Time: (1), 6 hr; (2), 6 hr, water continuously removed by anhydrous magnesium sulfate.

Curve 1 shows the formation of chromium(III) in the absence of a dehydrating agent (600 nm, maximum), curve 2 shows the spectrum of a stable chromium(V)-propylene glycol complex, II, free of chromium(III). These results were also confirmed by column chromatography using silica gel. Thus, under these conditions we were able to cease the second part of oxidation (eq. 1) which leads to decomposition of chromium(V) and formation of chromium(III). These results are also valid in case of ethylene glycol. A work is in progress to isolate both complexes in pure form.



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