theory by McGarvey.[15]

$$A_x = -K + P[\alpha_x - (g_0 - g_x)]$$

$$A_y = -K + P[\alpha_y - (g_0 - g_y)]$$

$$A_z = -K + P[\alpha_z - (g_0 - g_z)]$$

$$\alpha_x = \frac{-2}{7}(a^2 - b^2) - \frac{4}{7}\sqrt{3}ab\left(\frac{1 + (g_0 - g_z)}{8b^2}\right)\frac{-\sqrt{3}}{14} \times \frac{(a + b\sqrt{3})}{(a\sqrt{3} - b)}(g_0 - g_y)$$

$$\alpha_y = \frac{-2}{7}(a^2 - b^2) + \frac{4\sqrt{3}ab}{7}\left(\frac{1 + (g_0 - g_z)}{8b^2}\right)\frac{-\sqrt{3}}{14} \times \frac{(a - b\sqrt{3})}{(a\sqrt{3} + b)}(g_0 - g_x)$$

$$\alpha_z = \frac{4}{7}(a^2 - b^2) + \frac{\sqrt{3}}{14}\left[\frac{(a + b\sqrt{3})}{(a\sqrt{3} - b)}(g_0 - g_y) + \frac{(a - b\sqrt{3})}{(a\sqrt{3} + b)}(g_0 - g_x)\right]$$

$$P = g_0 g_n{}^{51}\beta\beta_n\langle r^{-3}\rangle$$

$$K = -g_0 g_n{}^{51}\beta\beta_n \frac{2}{3}\chi$$

For the A and g values given above we obtain $a = -0.999$, $b = 0.031$, indicating that the unpaired electron on the vanadium is almost entirely d_{z^2} in character, which strongly supports the structure proposed, as we would expect strong delocalization through the π-bonded Cp groups. The above equations differ from those of part 2[1] in the matter of signs. This is due to the fact that we have chosen a different z axis in the present paper. In part 2 the z axis was chosen to be perpendicular to the plane containing the V and Cp groups. In this paper, it is chosen along the line of centers of the V and Cp groups. In both cases it lies along the line of maximum electron density.

The $\langle 1/r^3\rangle$ value obtained is 1.80 au compared with values of over 2 for Cp_2VL_2 compounds[9] (L is a ligand). Comparison of the calculated P values with those obtained from Hartree–Fock $\langle r^{-3}\rangle$ values[16] shows that the effective nuclear charge on the vanadium changes from ca. +1.0 for Cp_2VCl_2[1] to +0.2 for the complex $Cp_2VH(\mu\text{-}Cl)_2AlX_2$. This decrease in effective nuclear charge as the structure changes from tetrahedral to trigonal bipyramidal is probably due in the main to the greater orbital overlap which occurs between the Cp groups and the vanadium in the latter structure.

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References and Notes

(1) Part 2: A. G. Evans, J. C. Evans, D. J. C. Espley, P. H. Morgan, and J. Mortimer, *J. Chem. Soc., Dalton Trans.*, 57 (1978).
(2) A. G. Evans, J. C. Evans, and E. H. Moon, *J. Chem. Soc., Dalton Trans.*, 2390 (1974).
(3) P. Cossee, *J. Catal.*, **3**, 80 (1964).
(4) G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, **10**, 105 (1971).
(5) D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc., Dalton Trans.*, 1972 (1972).
(6) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **76**, 4281 (1954).
(7) J. C. Evans, P. H. Morgan, and R. H. Renaud, *Anal. Chim. Acta, Comput. Ed.*, **2**, 175 (1978).
(8) J. E. Wertz and J. P. Bolton, "Electron Spin Resonance—Elementary Theory and Practical Applications", McGraw-Hill, New York, 1972.
(9) J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 6422 (1975).
(10) G. Henrici-Olive and S. Olive, *J. Organomet. Chem.*, **17**, 83 (1969).
(11) B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, **13**, 135 (1970).
(12) G. Henrici-Olive and S. Olive, *J. Organomet. Chem.*, **19**, 309 (1969).
(13) H. H. Brintzinger, *J. Am. Chem. Soc.*, **89**, 6871 (1967).
(14) L. J. Guggenberger and F. N. Tebbe, *J. Am. Chem. Soc.*, **95**, 7870 (1973).
(15) B. R. McGarvey, *Electron Spin Reson. Met. Complexes, Proc. Symp.* (1969).
(16) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

Synthesis of Stable Chromium(V) Complexes of Tertiary Hydroxy Acids[1]

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Abstract: Stable, water-soluble chromium(V) complexes of the general formula $Na[OCr(O_2COCR_1R_2)_2]$ were prepared in 60–90% yields by the reaction of anhydrous sodium dichromate in acetone with tertiary α-hydroxy acids (2-hydroxy-2-methylpropionic, 2-hydroxy-2-methylbutyric, 2-ethyl-2-hydroxybutyric, 2-butyl-2-hydroxyhexanoic, 1-hydroxycyclopentanecarboxylic, 1-hydroxycyclohexanecarboxylic, and 2-hydroxy-2-phenylpropionic acids). The stoichiometry of the reaction is $Na_2Cr_2O_7 + 5R_1R_2C(OH)CO_2H = 2Na[OCr(O_2COCR_1R_2)_2] + R_1R_2CO + CO_2 + 5H_2O$.

We recently reported[2] the synthesis of the first stable water-soluble chromium(V) compound, potassium bis(2-hydroxy-2-methylbutyrato)oxochromate(V), prepared from 2-hydroxy-2-methylbutyric acid and chromium trioxide in an aqueous solution. Since chromium(V) is formed in an equimolar mixture (eq 1) with chromium(III), isolation of the complex involves its separation on ion exchange resins, removal of large quantities of water, and careful balancing between solubility of individual components and stability of the product. It is a tedious, low-yield (20%) synthesis of a limited potential which succeeded mainly due to the ability of 2-hydroxy-2-methylbutyric acid to sufficiently stabilize the pentavalent chromium in water. In order to avoid these disadvantages, we

$$2Cr(VI) + 2C_2H_5(CH_3)C(OH)COOH \rightarrow Cr(V) + Cr(III) + 2CH_3CH_2COCH_3 + 2CO_2 \quad (1)$$

developed a simple, generally applicable route for the synthesis of chromium(V) complexes of tertiary α-hydroxy acids using acetone as a solvent.

Results and Discussion

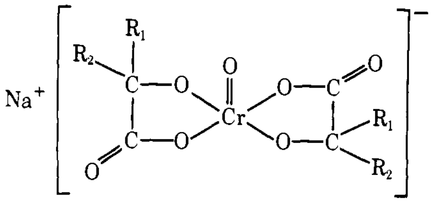
Anhydrous sodium dichromate reacts with 2-hydroxy-2-methylbutyric acid in acetone to yield sodium bis(2-hydroxy-2-methylbutyrato)oxochromate(V), methyl ethyl ketone, and carbon dioxide. The chromium(V) complex is formed in an essentially quantitative yield and is very stable (Figure 1); only traces of chromium(VI) can be detected at the end of the reaction. As chromium(V) is present in the form of a complex anion containing two molecules of the hydroxy acid per atom of chromium, the overall stoichiometry of the reaction is given by

$$\begin{aligned} &Na_2Cr_2O_7 + 5C_2H_5(CH_3)C(OH)COOH \\ &\quad\rightarrow 2Na[OCr(O_2COC(CH_3)C_2H_5)_2] \\ &\qquad + C_2H_5COCH_3 + CO_2 + 5H_2O \quad (2) \end{aligned}$$

Equation 2 requires 2.5 mol of the hydroxy acid for each mol of chromium(VI). Although it is possible to carry out the preparation of chromium(V) complexes in a strictly stoichiometric ratio, we preferred a 3:1 ratio of the hydroxy acids to chromium(VI). The excess of the substrate over sodium dichromate ensured a quantitative reduction of chromium(VI); subsequent crystallization of the complex from acetone–hexane completely removed excess hydroxy acid and oxidation products.

The product was identified by comparison of IR and UV spectra with potassium bis(2-hydroxy-2-methylbutyrato)oxochromate(V) monohydrate prepared in aqueous solutions by the previously reported method.[2] The UV spectra in aqueous solution were identical while the IR spectra (in Nujol) showed some differences. The ν(Cr=O) frequency was 1005 cm^{-1} for the sodium salt as compared with 994 cm^{-1} for the potassium salt; further, the potassium salt showed the presence of lattice water, ν(OH) 3400–3500 cm^{-1} (m), which was absent in the sodium salt. However, when the sodium salt was converted to the potassium salt on an ion exchange resin, identical IR spectra were obtained.

The same procedure, the reaction of a hydroxy acid with sodium dichromate in anhydrous acetone, was tested with a number of other compounds. Relatively well-defined chromium(V) complexes were obtained with 2-hydroxy-2-methylpropionic, 2-ethyl-2-hydroxybutyric, 2-butyl-2-hydroxyhexanoic, 1-hydroxycyclopentanecarboxylic, 1-hydroxycyclohexanecarboxylic, and 2-hydroxy-2-phenylpropionic acids. The products were identified by UV and IR spectra, elemental analysis, and iodometric determination of the valence state of chromium(V).[2] The results are consistent with the following structure.[2]



1, $R_1 = CH_3$; $R_2 = C_2H_5$
2, $R_1 = R_2 = CH_3$
3, $R_1 = R_2 = C_2H_5$
4, $R_1 = R_2 = C_4H_9$
5, R_1, $R_2 = (CH_2)_4$
6, R_1, $R_2 = (CH_2)_5$
7, $R_1 = CH_3$; $R_2 = C_6H_5$

Table I shows the effect of structural changes on solubility and stability of chromium(V) complexes. The complexes are soluble in water and acetone, but insoluble in nonpolar solvents. However, in the presence of crown ethers, the complexes can be dissolved in aromatic hydrocarbons. E.g., an approximately 0.1 M solution of **3** can be obtained in benzene containing 2% of 15-crown-5. With respect to the stabilities, unanticipated variations were encountered. While higher alkyl groups tend to stabilize the complex, phenyl groups have a strong destabilizing effect. 2-Hydroxy-2-phenylpropionic acid forms the least stable complex of those which we were able to prepare in pure form. 2-Hydroxy-2,2-diphenylacetic acid reacted readily with sodium dichromate in acetone to give a spectrophotometrically detectable chromium(V) complex, but all attempts to isolate the complex failed because of its instability. The rate of decomposition in aqueous solution is generally reduced by the presence of a small amount of the corresponding free hydroxy acid. This as well as the much greater stability in acetone suggests that the decomposition reaction[2] (predominantly disproportionation to chromium(VI) and chromium(III), accompanied by some ligand oxidation) is preceded by hydrolysis. All chromium(V) complexes are astonishingly resistant toward thermal decomposition. They do not show melting points, but slowly decompose to form chromium(III).

When citric and oxalic acids were allowed to react with sodium dichromate, a similar behavior was observed in the initial stage of the reaction. Isolation of the chromium(V) complexes in pure form, however, did not succeed because of their rapid reduction to chromium(III). Similarly, the formation of chromium(V) intermediates has also been observed spectrophotometrically in the oxidation of primary and secondary hydroxy acids (glycolic, glyoxylic, tartaric, malic, mandelic), unsaturated (maleic), and dicarboxylic (malonic, methyl-

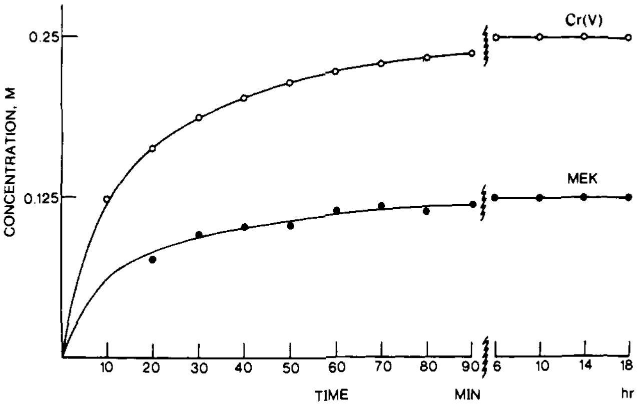


Figure 1. Time dependence of the formation of sodium bis(2-hydroxy-2-methylbutyrato)oxochromate(V) and methyl ethyl ketone (MEK) in acetone. Conditions: initial chromium(VI) = 0.25 M, 2-hydroxy-2-methylbutyric acid = 0.75 M, t = 25 °C.

Table I. Solubilities and Stabilities of Chromium(V) Complexes of Tertiary α-Hydroxy Acids $R_1R_2C(OH)COOH$

complex		solubility[a]		degree of decomposition,[b] %		dec point,[e]
R_1	R_2	water	acetone	in H_2O	in 0.1 M solutions of hydroxy acids	°C
CH_3	C_2H_5	290	103	58	13	180
CH_3	CH_3	270	4.1	81	64	180
C_2H_5	C_2H_5	190	203	28	2	180
C_4H_9	C_4H_9	16	87	27	c	180
$(CH_2)_4$		204	730	100	53	170
$(CH_2)_5$		340	710	100	13	170
CH_3	C_6H_5	170	810	100[d]	100[d]	140

[a] g/L, 25 °C. [b] 0.01 M solutions of chromium(V) complexes; 24 h at 25 °C. [c] 2-Butyl-2-hydroxyhexanoic acid is insoluble in water. [d] Decomposed completely in less than 1 h. [e] In a melting point capillary, with the temperature raising 1 °C/min.

malonic) acids. These chromium(V) complexes were also too unstable to be isolated.

The mechanism of the reaction in acetone is obviously different from that one in water.[3] The absence of chromium(III) formation suggests that the reaction between chromium(VI) and the hydroxy acids in acetone does not involve a three-electron oxidation-reduction step.[4] The formation of chromium(V) could be explained in terms of two consecutive one-electron reactions

Scheme I

$$\mathrm{Cr(VI)} + \mathrm{S} \rightarrow \mathrm{Cr(V)} + \mathrm{R}\cdot \tag{3}$$

$$\mathrm{Cr(VI)} + \mathrm{R}\cdot \rightarrow \mathrm{Cr(V)} + \mathrm{P} \tag{4}$$

or as an initial two-electron oxidation leading to the formation of chromium(IV) followed by a subsequent oxidation of chromium(IV) to chromium(V):

Scheme II

$$\mathrm{Cr(VI)} + \mathrm{S} \rightarrow \mathrm{Cr(IV)} + \mathrm{P} \tag{5}$$

$$\mathrm{Cr(VI)} + \mathrm{Cr(IV)} \rightarrow 2\mathrm{Cr(V)} \tag{6}$$

The latter type of reaction sequence has been ruled out for aqueous solutions.[5] However, the relative oxidation potentials in acetone may be sufficiently different to allow its consideration for this particular system.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 521 grating spectrophotometer in Nujol. Ultraviolet spectra were obtained on a Cary Model 15 recording spectrophotometer. Carbon and hydrogen microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. Sodium was determined by flame emission on a Perkin-Elmer Model 305B atomic absorption spectrophotometer using sodium chloride as the calibration standard. Water was determined by NMR technique on a Varian Model A-60D spectrometer.

Materials. Commercially available 2-hydroxy-2-methylpropionic acid (Eastman), 2-hydroxy-2-methylbutyric acid (Aldrich), 2-ethyl-2-hydroxybutyric acid (Aldrich), 1-hydroxycyclohexanecarboxylic acid (Pfaltz & Bauer), cadmium iodide (Merck, Reagent), magnesium (Fisher), butyl bromide (Fisher, Certified), and ethyloxalyl chloride (Aldrich) were used as received. 1-Hydroxycyclopentanecarboxylic acid (Pfaltz and Bauer) was recrystallized from acetone-hexane (mp 103-104 °C, lit.[6] 103 °C). 2-Hydroxy-2-phenylpropionic acid hemihydrate (95%, Aldrich) was recrystallized from acetone-hexane and the product dried in vacuo at 100 °C for about 30 min to remove crystalline water (mp 92-93 °C, lit.[7] 93-95 °C). Anhydrous sodium dichromate was obtained from the commercially available monohydrate (Baker Analyzed) by drying in vacuo at 100 °C to constant weight (about 30-40 min). Acetone (Fisher, spectroscopic grade) was dried over molecular sieves (Fisher, Type 4A). Hexane (Fisher, spectroscopic grade), diethyl ether (Corco, Reagent), 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5, Aldrich), and deuterium oxide (Bio-Rad Laboratories, 99.8% D_2O) were used as received.

Analytical Procedures. The valence state of chromium in all complexes was confirmed[2] iodometrically (a) directly and (b) after oxidizing all chromium to chromium(VI) by hydrogen peroxide in alkaline solution.[8] A 1:1.46 to 1:1.53 ratio for (a):(b) is in good agreement with the theoretical ratio of 1:1.50 for pentavalent chromium.

Chromium(V). Solid samples (0.006-0.008 g) were analyzed iodometrically.[8] Chromium(V) was first quantitatively converted[2] to chromium(VI) by dissolving the sample in about 2-3 mL of 2 M aqueous sodium hydroxide; the solution was acidified with 4 M HCl and titrated.

Chromium(VI). The presence of chromium(VI) in chromium(V) was detected spectrophotometrically using a modified iodometric method recently developed.[3] A small amount of a solid sample (less than 1 mg) was introduced to a buffer solution of potassium iodide (2 mL) in a photometric cell and analyzed as described. The chromium(VI) content was determined from a relative ratio of Cr(VI):Cr(V).

Methyl Ethyl Ketone. A reaction solution (1-2 mL) was diluted with about 5 mL of water and passed through a column containing anion exchange resin (Dowex 2-X8 in Cl^- form, 20-50 mesh) to completely remove chromium(V) and chromium(VI), and the eluate was analyzed by LC using a Waters Associates Model M-6000A liquid chromatograph equipped with a Model 440 absorbance detector (254 nm), C_{18} reverse phase column, and water-methanol-acetic acid (16:4:1 v/v) as a solvent system. The yield of methyl ether ketone was calculated from a calibration graph. Other corresponding ketones (except acetone) were detected by GLC in hexane-acetone solutions after the removal of chromium(V) and identified by comparison with authentic samples.

Water. In a typical experiment, about 0.07-0.09 g of a chromium(V) complex was dissolved in about 0.6-0.7 mL of deuterium oxide, the solution was subjected to molecular distillation on a vacuum line, and volatile material was trapped in an ethanol-dry ice bath. Deuterium oxide quantitatively recovered (99.3-99.7%) was analyzed by NMR using standard addition technique. The content of water present in the sample (corrected for the original contamination of deuterium oxide by water) was calculated according to

$$\mathrm{H_2O}\ (\%) = \frac{h_1 - h_0}{h_1' - h_1} \frac{g_t}{g_{\mathrm{NMR}}} \frac{g_{\mathrm{H_2O}}}{g_s} 100 \tag{7}$$

where h_0, h_1, and h_1' are integrated proton intensities of deuterium oxide (99.8% D_2O), deuterium oxide recovered by molecular distillation, and the same sample after addition of a known amount of water, respectively, g_t is the amount of deuterium oxide used, g_{NMR} is the amount of deuterium oxide weighed into the NMR tube after the molecular distillation, $g_{\mathrm{H_2O}}$ is the amount of water injected with a Hamilton syringe to g_{NMR} (usually 5 μL), and g_s is the amount of the chromium(V) sample analyzed.

Synthesis of Chromium(V) Complexes. The synthesis was carried out in 25- or 50-mL Erlenmeyer flasks fitted with a ground-glass stopper. The progress of the reaction was followed spectrophotometrically at 750 nm by transferring a small amount of the solution to a photometric cell (0.1-0.2 cm) of a Cary Model 15 spectrophotometer equipped with a thermostated cell holder. As the wavelength of 750 nm is specific[3] for chromium(V), its formation in the presence of chromium(VI) was followed directly from the time-absorbance curve. A detailed procedure is given for preparation of only one chromium(V) complex, as the method is fairly general, and requires only minor modifications for the synthesis of other complexes.

Sodium Bis(2-hydroxy-2-methylbutyrato)oxochromate(V) (1). 2-Hydroxy-2-methylbutyric acid (3.60 g, 30 mmol) was dissolved in 40 mL of acetone, 1.3 g (5.0 mmol) of finely pulverized anhydrous sodium dichromate added, and the heterogeneous mixture stirred until the salt was completely dissolved (7-10 min). The resulting dark red-brown solution was allowed to react for 26 h at 25 °C. Addition of 100 mL of hexane led to the separation of the chromium(V) complex as a heavy, dark oil which slowly crystallized. Partially oily product was washed twice with 5 mL of hexane and volatile material (solvents, methyl ethyl ketone, and water) were removed in vacuo at room temperature, leaving an essentially quantitative yield of solid product. The chromium(V) complex was further purified by crystallization to remove 2-hydroxy-2-methylbutyric acid. The crude product was dissolved in 40 mL of acetone, 100 mL of hexane was added, and the complex precipitated out as a dark oil. Upon standing (15-20 min), the oil solidified and formed dark red-brown crystals. The crystals were washed with hexane and dried in vacuo at room temperature to constant weight (25-30 min), affording 2.63 g (8.1 mmol, 81%) of **1**: IR (Nujol) 1689 (s, br), 1337 (m), 1317 (m), 1256 (m), 1192 (m), 1168 (m), 1129 (w), 1042 (w), 1028 (w), 1004 (m), 934 (m), 904 (w), 934 (m), 802 (w), 755 (w), and 704 (m) cm^{-1}; UV (H_2O) λ nm (ε) 250 (6420), 350 (1208), 491 min (164), 510 max (170), 646 min (34.3), 733 max (41.8), 750 (41.5), and 800 (35.0).

Anal. Calcd for $C_{10}H_{16}CrNaO_7$: C, 37.16; H, 4.99; Cr, 16.09; Na, 7.11. Found: C, 37.45; H, 5.12; Cr, 15.9; Na, 7.0. Cr(VI) content: 0.3% of total Cr.

Sodium Bis(2-hydroxy-2-methylpropionato)oxochromate(V) (2). To a solution of 1.56 g (15.0 mmol) of 2-hydroxy-2-methylpropionic acid in 40 mL of acetone was added 0.655 g (2.50 mmol) of sodium dichromate. The mixture was stirred to dissolve the salt (5-7 min) and kept for 24 h at 25 °C. As this chromium(V) complex is not very soluble in acetone, some crystalline product was already formed at the end of the reaction. Addition of 80 mL of hexane led to further precipitation of dark red-brown crystals giving 1.32 g (4.49 mmol, 90%)

of **2**: IR (Nujol) 1698 (s, br), 1291 (s), 1189 (s, br), 1151 (w, sh), 995 (m), 867 (s), 896 (w), 833 (s), 772 (w), and 725 (s) cm^{-1}; UV (H_2O) λ nm (ϵ) 250 (6320), 350 (1295), 486 min (164), 512 max (173), 750 (35.6), and 800 (31.6).

Anal. Calcd for $C_8H_{12}CrNaO_7$: C, 32.55; H, 4.10; Cr, 17.61; Na, 7.79. Found: C, 32.91; H, 4.20; Cr, 17.4; Na, 7.5. Cr(VI) content: 0.6% of total Cr.

Sodium Bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) **Monohydrate** (**3**). 2-Ethyl-2-hydroxybutyric acid (1.98 g, 15.0 mmol) was dissolved in 20 mL of acetone, 0.65 g (2.50 mmol) of sodium dichromate added, the mixture stirred, and the dark red solution allowed to react for 26 h at 25 °C. Addition of 50 mL of hexane led to instant formation of deep red-violet crystals of the chromium(V) complex in essentially quantitative yield. Recrystallization from acetone-hexane afforded 1.42 g (3.85 mmol, 77%) of **3**: IR (Nujol) 3510 (m, br), 1680 (s, br), 1312 (m), 1257 (m), 1177 (m), 1045 (w), 998 (m), 961 (s), 888 (w), 845 (m), 815 (w), and 712 (m) cm^{-1}; UV (H_2O) λ nm (ϵ) 250 (6510), 350 (1200), 485 min (160), 510 max (168), 633 min (28.6), 740 max (40.9), 750 (40.7), and 800 (39.4).

Anal. Calcd for $C_{12}H_{22}CrNaO_8$: C, 39.03; H, 6.01; Cr, 14.08; Na, 6.23; H_2O, 4.88. Found: C, 39.42; H, 6.00; Cr, 14.1; Na, 6.6; H_2O, 5.3. No Cr(VI) was detected.

2-Butyl-2-hydroxyhexanoic acid. The acid was prepared from dibutylcadmium and ethyloxalyl chloride using a procedure described by Stacy and McCurdy[9] with minor modifications. A solution of butylmagnesium bromide, prepared from 10 g (0.41 mol) of magnesium and 54.6 g (0.40 mol) of butyl bromide in 100 mL of diethyl ether, was added to 73.2 g (0.20 mol) of cadmium iodide in 100 mL of diethyl ether. The reaction mixture was refluxed for about 30 min and then slowly added to 25 g (0.18 mol) of ethyloxalyl chloride in 100 mL of diethyl ether. After short reflux (about 30 min) the product was decomposed with water and diluted hydrochloric acid (10%) and extracted with diethyl ether, the organic layer separated, and the diethyl ether removed by distillation. The crude oily product was refluxed with 100 mL of 4 M aqueous sodium hydroxide for 3 h, then acidified with 130 mL of 4 M hydrochloric acid, upon which a solid separated. The solid was extracted with hexane and twice crystallized to give 16.1 g (0.085 mol, 47% yield) of 2-butyl-2-hydroxyhexanoic acid, mp 85-86 °C (lit.[9] 87.5 °C).

Sodium Bis(2-butyl-2-hydroxyhexanoato)oxochromate(V) **Monohydrate** (**4**). To a solution of 2.82 g (15.0 mmol) of 2-butyl-2-hydroxyhexanoic acid in 20 mL of acetone was added 0.65 g (2.5 mmol) of sodium dichromate. The mixture was stirred for about 5 min to dissolve the dichromate, and the solution kept for 20 h at 25 °C. Addition to 160 mL of hexane resulted in the separation of a dark red-brown oil, which was dried in vacuo and crystallized from acetone-hexane to yield 1.52 g (3.16 mmol, 63%) of **4**: IR (Nujol) 3450 (s, br), 1680 (s, br), 1345 (w), 1257 (m), 1225 (w), 1158 (m), 1000 (m), 913 (w), 850 (m), 814 (w), and 725 (m, br) cm^{-1}; UV (H_2O) λ nm (ϵ) 250 (6880), 350 (1362), 489 min (195), 506 max (199), 638 min (31.8), 739 max (39.7), 750 (39.6), 800 (34.1).

Anal. Calcd for $C_{20}H_{38}CrNaO_8$: C, 49.89; H, 7.96; Cr, 10.80; Na, 4.77; H_2O, 3.74. Found: C, 50.34; H, 7.46; Cr, 10.4; Na, 4.5; H_2O, 3.9. No Cr(VI) was detected.

Sodium Bis(1-hydroxycyclopentanecarboxylato)oxochromate(V) **Monohydrate** (**5**). To a solution of 0.98 g (7.5 mmol) of 1-hydroxycyclopentanecarboxylic acid in 10 mL of acetone was added 0.327 g (1.25 mmol) of sodium dichromate, the mixture stirred, and the dark brown solution allowed to react for 8 h at 25 °C. After the addition of 40 mL of hexane, the crude chromium(V) complex separated as a dark oil which, after 10-15 min, began to form dark red-brown crystals. Recrystallization from acetone-hexane yielded 0.77 g (2.11 mmol, 84%) of **5**: IR (Nujol) 3440 (m, br), 1678 (s), 1334 (m), 1317 (m), 1173 (m), 1070 (m), 1001 (m), 949 (w), 891 (w), 841 (m), and 725 (m) cm^{-1}; UV (H_2O) λ nm (ϵ) 250 (7361), 350 (1495), 500 min (227), 519 max (229), 750 (42.6), and 800 (38.0).

Anal. Calcd for $C_{12}H_{18}CrNaO_8$: C, 39.46; H, 4.97; Cr, 14.23; Na, 6.29; H_2O, 4.93. Found: C, 39.93; H, 4.76; Cr, 14.3; Na, 6.6; H_2O, 4.6. Cr(VI) content: 1.5% of total Cr.

Sodium bis(1-hydroxycyclohexanecarboxylato)oxochromate(V) (**6**) was prepared in a similar manner from 1-hydroxycyclohexanecarboxylic acid (0.65 g, 4.5 mmol) and sodium dichromate (0.197 g, 0.75 mmol) in 10 mL of acetone. Recrystallization from acetone-hexane gave 0.37 g (0.99 mmol, 66%) of dark brown crystals of **6**: IR (Nujol) 1678 (s, br), 1229 (s, br), 1271 (m), 1232 (w), 1201 (w), 1151 (w), 1074 (m), 1060 (w, sh), 993 (m), 967 (s), 844 (m), 824 (w), and 744 (m, br) cm^{-1}; UV (H_2O) λ nm (ϵ) 250 (6070), 350 (1280), 520 sh (207), 750 (41.7), and 800 (39.1).

Anal. Calcd for $C_{14}H_{20}CrNaO_7$: C, 44.81; H, 5.37; Cr, 13.85; Na, 6.13. Found: C, 44.94; H, 5.65; Cr, 13.4; Na, 6.4. Cr(VI) content: 1.1% of total Cr.

Sodium bis(2-hydroxy-2-phenylpropionato)oxochromate(V) (**7**) was prepared from anhydrous 2-hydroxy-2-phenylpropionic acid (0.62 g, 3.7 mmol) and sodium dichromate (0.163 g, 0.62 mmol) in 10 mL of acetone. After the reaction proceeded for 5 h at 25 °C, 20 mL of hexane was added, resulting in the separation of a dark brown oil which was washed with hexane and dried in vacuo to yield 0.32 g (0.74 mmol, 60%) of **7** as a brown powder. Attempts to crystallize the material failed: IR (Nujol) 1680 (s, br), 1275 (m), 1227 (w), 1131 (m), 1069 (m), 997 (m), 940 (m), 893 (m), 819 (w), 739 (w, sh), 725 (m), and 700 (m) cm^{-1}; UV (H_2O) λ nm (ϵ) 260 (7160), 350 (1345), 520 sh (128), 700 sh (42.1), 750 (40.3), and 800 (36.9).

Anal. Calcd for $C_{18}H_{16}CrNaO_7$: C, 51.56; H, 3.85; Cr, 12.40; Na, 5.48. Found: C, 51.12; H, 4.25; Cr, 11.6; Na, 6.0. Cr(VI) content: 4% of total Cr.

References and Notes

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(2) M. Krumpolc, B. G. DeBoer, and J. Roček, *J. Am. Chem. Soc.*, **100**, 145 (1978).
(3) M. Krumpolc and J. Roček, *J. Am. Chem. Soc.*, **99**, 137 (1977).
(4) K. G. Srinivasan and J. Roček, *J. Am. Chem. Soc.*, **100**, 2789 (1978), and references cited therein.
(5) M. Rahman and J. Roček, *J. Am. Chem. Soc.*, **93**, 5462 (1971).
(6) B. Tchoubar and C. Collin, *Bull. Soc. Chim. Fr.*, 680 (1947).
(7) "Handbook of Chemistry and Physics", 50th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1969.
(8) I. M. Kolthoff and R. Belcher in "Volumetric Analysis", Vol. III, Interscience, New York, 1965, p 332.
(9) G. W. Stacy and R. M. McCurdy, *J. Am. Chem. Soc.*, **76**, 1914 (1954).