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A Stable Chromium(V) Compound. Synthesis, Properties, and Crystal Structure of Potassium Bis(2-hydroxy-2-methylbutyrato)oxochromate(V) Monohydrate[1]

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Abstract: The first stable water-soluble chromium(V) compound, potassium bis(2-hydroxy-2-methylbutyrato)oxochromate(V) monohydrate, K[OCr(O$_2$CCOMeEt)$_2$]·H$_2$O, was prepared in crystalline form from chromium trioxide and 2-hydroxy-2-methylbutyric acid; its spectral (UV, ESR, IR) properties and other physical data are given. The stability of the compound is discussed. A bicyclic structure proposed on the basis of the elemental composition and spectral data was confirmed by x-ray diffraction. The compound crystallizes in the noncentrosymmetric monoclinic space group *Cc* with lattice parameters $a = 12.362$ (6), $b = 16.665$ (9), $c = 7.611$ (3) Å, $\beta = 90.33$ (3)°, $V = 1567.9$ (13) Å^3. For $Z = 4$ and formula weight 357.35, ρ (calcd) $= 1.514$ g cm^{-3}, ρ (obsd) $= 1.518$ (5) g cm^{-3}. The 736 data were collected from a small, fractured crystal using an autodiffractometer and Mo Kα radiation (2θ (max) $= 40°$) and the structure refined to $R(F) = 7.06\%$ and $R(wF) = 6.79\%$. The anion geometry is very similar to those found for isoelectronic VO^{2+} complexes (Cr–O $= 1.554$ (14) Å) and is intermediate between square pyramidal and trigonal bipyramidal.

The preparation of stable chromium(V) compounds is of considerable importance not only to chemistry, but also to nuclear physics. For many years, chemists have been aware of the crucial role of these intermediates in all known mechanisms[3] of chromium(VI) oxidations. The interest of nuclear physicists stems from the observation that chromium(V) complexes in media of high hydrogen content are among the most efficient paramagnetic species available for the preparation of dynamically polarized proton targets needed in the study of high-energy particle interactions.[4–7]

The first observation indicating the formation of chromium(V) complexes in the course of oxidation of several organic acids (oxalic, lactic, citric) by potassium dichromate in glacial acetic acid was reported by Kon.[8,9] Higher concentrations of relatively more stable chromium(V) complexes were prepared by the reduction of potassium dichromate by glycerol,[10] ethylene glycol,[11,12] dithioethylene glycol,[13] several phenol derivatives,[14] diethylene glycol,[15] and 1,2-propanediol.[16]

None of these studies, however, resulted in isolation of a stable, well-characterized chromium(V) compound. A survey of the literature of pentavalent chromium reveals that relatively few compounds of known composition have been prepared, mostly derivatives of oxo species CrO$_4$$^{3-}$, Cr(O$_2$)$_4$$^{3-}$, and CrO^{3+}. The anions are known to form hypochromates M$_3$^{I}CrO$_4$ (M = Li, Na),[17] M$_3$^{II}[(CrO$_4$)$_2$], M$_5$^{II}[(CrO$_4$)$_3$OH] (M = Ca, Sr, Ba),[18] and peroxides M$_3$^{I}[Cr(O$_2$)$_4$] (M = NH$_4$, Na, K).[19] Derived from the oxocation CrO^{3+} and the related anions CrOX$_4$$^-$ and CrOX$_5$$^{2-}$ (X = F, Cl) are the oxotrichloride CrOCl$_3$,[20] perfluoropinacolates M^I[CrO(pfp)$_2$] (M = K, Cs, Et$_4$N),[21] fluorooxo complexes M^I[CrOF$_4$] (M = K, Ag)[22] and (Et$_4$N)$_2$[CrOF$_5$],[23] chlorooxo complexes M^I-[CrOCl$_4$] (M = Me$_4$N, Et$_4$N, Pr$_4$N, Bu$_4$P, Ph$_4$As, BzPh$_3$P)[23] and M$_2$^{II}[CrOCl$_5$] (M = NH$_4$, K, Rb, Cs),[24] and binary salts (the "Weinland complexes") of the types RNH-[CrOCl$_4$],[20,25,26] [RNCOR][CrOCl$_4$],[20] and [NHRNH]-[CrOCl$_5$][20] with nitrogen bases (pyridine, quinoline, *o*-phenanthroline, etc.). Other chromium(V) compounds reported in the literature are the oxide Cr$_2$O$_5$,[27] the fluoride CrF$_5$,[28] dibenzoatotrichlorochromium(V)[20] (C$_6$H$_5$CO$_2$)$_2$CrCl$_3$, and the chlorooxo complexes Cs$_2$[CrO(AB)Cl$_3$] (AB = anions of tartaric, hydroxymalonic, and malic acids).[23] All these compounds (except peroxides[29] and perfluoropinacolates, which are insoluble in water[21]) are characterized by their high instability with respect to hydrolytic decomposition. Although

some of these have been known for a fairly long time, little is known about their chemical properties.

We have previously reported that a relatively stable chromium(V) species was observed as an intermediate in the chromic acid oxidation of aqueous solutions of oxalic[30] or glycolic[31] acids. Our recent observation that a particularly stable chromium(V) intermediate is formed in the chromic acid oxidation of a tertiary α-hydroxy acid, 2-hydroxy-2-methylbutyric acid,[32,33] encouraged us to attempt to obtain this intermediate in pure form.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Model 521 spectrophotometer using Nujol mull technique. Ultraviolet spectra were measured on a Cary Model 15 recording spectrophotometer in 0.1–5.0-cm cells. ESR spectra were recorded on a Japan Electron Optics Lab. Co., Ltd., Spectrometer, Model JES-3BSX, and g values were measured by reference to di-*tert*-butyl nitroxide (DTBN, g = 2.0065). Magnetic susceptibility of the chromium(V) complex was determined by the Gouy method using aqueous Cs_2CoCl_4 as the calibration standard and the raw data were corrected for the diamagnetism of water.[34] Carbon and hydrogen microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. Analyses for chromium were carried out by standard iodometric technique[35] and by flame absorption on a Perkin-Elmer Model 305 B atomic absorption spectrophotometer using potassium dichromate as the calibration standard. Potassium was determined gravimetrically as potassium perchlorate[36] and by flame emission using potassium chloride as the calibration standard. A Fisher Accumet pH meter, Model 19, fitted with a Fisher Microprobe combination electrode was used for pH measurements.

Materials. 2-Hydroxy-2-methylbutyric acid (Aldrich) was recrystallized from hexane and estimated to be 99% pure by GLC (mp 72–73 °C). Commercially available reagent grade chromium trioxide (Fisher), perchloric acid (B&A reagent), potassium hydrogen carbonate (Fisher), and hexane (Fisher, spectroscopic grade) were used as received. Acetone (Fisher, spectroscopic grade) was dried over molecular sieves (Fisher, Type 4A).

Potassium Bis(2-hydroxy-2-methylbutyrato)oxochromate(V). The best results were obtained by the following procedure: 5 mL of 2 M 2-hydroxy-2-methylbutyric acid (10 mmol), 5 mL of 2 M perchloric acid (10 mmol), 1 mL of 2 M chromium trioxide (2 mmol), and 9 mL of water were mixed at room temperature and placed in a freezer at −16 °C. In 2 or 3 days[37] the reaction mixture was brought to room temperature and rapidly passed through a cation-exchange resin (Dowex 50-X8, 50-100 mesh) in the hydrogen ion form in order to remove a dark blue chromium(III) species. Solid potassium hydrogen carbonate was added (1.2–1.3 g, 12–13 mmol) to neutralize perchloric acid and part of the 2-hydroxy-2-methylbutyric acid; the solution must be kept somewhat acidic (pH ~4) by only partial neutralization of the hydroxy acid in order to stabilize the chromium(V) compound. The precipitate of potassium perchlorate was filtered off, the filtrate (about 20 mL) divided into two portions, and each portion evaporated to dryness in a stream of air on a water bath at 45 °C. This operation was carried out as fast as possible (about 30 min) in order to minimize losses caused by slow reductive decomposition of the chromium(V) compound. The resulting dark oil containing the chromium(V) compound together with excess hydroxy acid and its potassium salt, potassium perchlorate, a small amount of chromium(III), and some remaining water, slowly turned into a solid. Both portions of the crude chromium(V) salt were successively extracted with a total of 5 mL of acetone and the extracts combined. Addition of hexane (25–30 mL) resulted in the separation of the crude chromium(V) compound, usually in the form of a dark oil. In order to completely remove the remaining hydroxy acid, the oily product was dissolved in about 3 mL of acetone, reprecipitated by the addition of 20–25 mL of hexane, and dried under vacuum for a few minutes to evaporate acetone and water and induce solidification.

The dark brown solid (about 0.40 g) was further purified by column chromatography on silica gel (5 g, 60-200 mesh) with hexane–acetone (1:1) in order to remove chromium(III) and the last traces of potassium salts and water. Precipitation by the addition of hexane yielded about 0.12–0.14 g (0.35–0.40 mmol) of a red-brown oil which slowly solidified into prismatic crystals of potassium bis(2-hydroxy-2-

methylbutyrato)oxochromate(V) monohydrate in a 35–40% overall yield (based on eq 1). Anal. Calcd for $C_{10}H_{18}CrKO_8$: C, 33.6; H, 5.1; Cr, 14.5; K, 10.9. Found: C, 33.9; H, 5.0; Cr, 14.5; K, 10.8.

Crystals used for x-ray analysis were prepared by slowly dropping hexane into an acetone solution of the chromium(V) salt at room temperature. As soon as the solution became cloudy, it was placed in a freezer (−16 °C) for 1 day. The crystals (size 0.5–2 mm) were washed with hexane and dried at room temperature by exposure to a stream of air.

X-Ray Crystal Structure Determination.[38] Most of the material was polycrystalline and of such fragility that all attempts to isolate single crystals only pulverized them. However, a number of much smaller, apparently monocrystalline, quadrilateral prisms were also present. Since these had a color and density indistinguishable from those of the polycrystalline material, and appeared to have a closely related morphology, they were presumed to be the same substance. Subsequently a powder diffraction photograph of the bulk material verified this assumption. That both types of crystal were apparently unchanged after several weeks' exposure to laboratory air again testifies to the remarkable stability of this chromium(V) complex.

One of the small crystals was selected and glued to the tip of a glass fiber (itself fixed in a brass pin) with its elongated c direction parallel to the fiber. Precession camera photographs (zero level, first level, and cone-axis photographs normal to both a and b) provided approximate unit cell dimensions, displayed $2/m$ Laue symmetry, and revealed systematic absences of $h + k \neq 2n$ for all hkl and $l \neq 2n$ for $h0l$, consistent with the monoclinic space groups $C2/c$ and Cc.

The crystal was transferred to a Picker FACS-1 autodiffractometer which was employed to obtain the more precise unit cell dimensions listed in Table I. Narrow-source, open-counter ω scans were performed on several reflections, with the result that while $hk0$ reflections (at small χ angles) displayed normal, narrow peak shapes [full width at $\frac{1}{10}$ maximum (fwtm) = 0.4°], the $00l$ reflections (near χ = 90°) consisted of at least three peaks with separations up to 0.8° and fwtm up to 1.3°. This observation would normally cause the immediate rejection of the sample. However, since considerable effort, not described here, had already been expended in obtaining a crystal even this good, and the probability of obtaining an appreciably better one with any reasonable additional effort seemed small, we elected to collect intensity data from this sample and accept a less precise structure determination than would otherwise be expected. Accordingly, intensity data were collected, using the same instrument, and converted to $|F_o|$ values as outlined in Table I and more fully described elsewhere.[39]

A three-dimensional Patterson function gave coordinates for the chromium and potassium atoms and strongly indicated that the noncentrosymmetric space group, Cc, was correct. Successive application of least-squares refinements[40] and difference-Fourier syntheses gave the positions of the remaining nonhydrogen atoms and confirmed the choice of space group. Least-squares refinement of a model, which included the positions of all 20 nonhydrogen atoms, anisotropic thermal parameters for the chromium and potassium atoms, isotropic thermal parameters for the remainder, and a single scale factor, converged with $R(F)$ = 9.14% and $R(wF)$ = 8.88%. However, the flaws in the data were clearly having a serious effect in that there were unreasonably large disagreements between chemically equivalent bond lengths. A difference-Fourier synthesis was calculated and displayed regions of positive density (up to 0.70 e Å^{-3}) which were disposed in pairs about nearly every atomic position and oriented in the $\pm z$ direction. These were clearly associated with the errors in the data due to the fractured nature of the crystal (shown by the ω scans described above), since they are expected to be most serious for reflections lying near $00l$.

A means of accounting for these errors, and thereby diminishing their effect, was sought. This took the form of an anisotropic scale factor which varied smoothly with direction in reciprocal space, but was independent of the radial coordinate, $2\lambda^{-1} \sin \theta$. The latter condition was imposed both to minimize correlations with thermal parameters and because the fraction of a reflection's intensity which is "missed" in a 2θ scan due to ω splitting should be independent of that reflection's 2θ (center) value. The least-squares program was modified to replace the usual single scale factor (as a multiplier of $|F(\text{calcd})|$) with the form $2\lambda^{-1} \sin \theta \ [s_{11}h^2a^{*2} + s_{22}k^2b^{*2} + s_{33}l^2c^{*2} + 2s_{12}hka^*b^* + 2s_{13}hla^*c^* + 2s_{23}klb^*c^*]^{-1/2}$ and to include the s_{ij} among the adjustable parameters. This form produces scale factors distributed as the radii of an ellipsoid in reciprocal space. Continued

refinement with this modification[42] substantially reduced the discrepancy ratios to $R(F) = 7.50\%$ and $R(wF) = 7.44\%$. A separate run, employing the reciprocal of the above form (scale factors distributed as the projections of an ellipsoid upon reciprocal space radius vectors), gave effectively identical R values and interatomic distances. The direct form was arbitrarily chosen for use in all subsequent refinement cycles. We emphasize that employing such an anisotropic scale factor is a purely ad hoc procedure and is justified only by the need to somehow minimize the effect of the systematic errors in the data upon the parameters of interest. It can have no place whatever in the analysis of data sets not known to be affected by similar errors.

Prior to the introduction of the anisotropic scale factor, paired refinements which included anomalous dispersion effects had failed to discriminate between the two possible orientations of the atomic arrangement relative to the measured set of reflections. After the change, the correct orientation was clearly indicated by its better agreement ($R(wF) = 7.43\%$ vs. 7.49%)[43] and by its more nearly equal chromium-light atom distances.[44]

Hydrogen atoms were now introduced in calculated positions. For the methyl and ethyl groups, C–H distances[45] of 0.95 Å, tetrahedral angles, and staggered orientations were assumed. The two hydrogen atoms of the water molecule were placed 1.0 Å from the water oxygen atom (W), collinear with W···O(4) and with W···O(7). Every hydrogen atom was assigned an isotropic thermal parameter 1.0 Å^2 greater than that of the atom to which it is bonded. In all subsequent least-squares cycles, the shifts of all hydrogen atom parameters were constrained to be equal to the shift in the corresponding parameter of the bonded carbon (or water oxygen) atom (i.e., *zero* additional adjustable parameters). After inspecting the data for evidence of secondary extinction effects (none was found) and correcting[39] the eight lowest angle reflections for the effect of the niobium β filter, the model was refined to convergence, yielding the final values of $R(F) = 7.06\%$ and $R(wF) = 6.79\%$.

The final estimated standard deviation of an observation of unit weight (or goodness of fit parameter), defined by $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.84, where the number of data, m, was 736 and the number of adjustable parameters, n, was 94 ($m/n = 7.83$). This function appeared to be independent of $|F_o|$ and $\lambda^{-1} \sin \theta$, so the weighting scheme was deemed acceptable. In the final least-squares cycle, no positional parameter shifted by more than 0.12 of the standard deviation calculated for it, and no other parameter by more than 0.24σ. A final difference Fourier synthesis had as its maximum a peak of height 0.58 e Å^{-3} and did not show the systematically paired peaks seen previously.

Final values of the anisotropic scale factor parameters were $S_{11} = 3.54$ (9), $S_{22} = 3.30$ (9), $S_{33} = 5.11$ (15), $S_{12} = -0.02$ (6), $S_{13} = -0.52$ (9), and $S_{23} = 1.09$ (11). This matrix produces scale factors which display a maximum to minimum ratio of 1.31, which are nearly constant in the $hk0$ plane, and indicates that reflections near $00l$ were represented by as little as 58% of their "true" intensities. As expected, many of the S_{ij} had substantial, but by no means intolerable, negative correlation coefficients with the correspondingly subscripted anisotropic thermal parameters of the chromium and potassium atoms. The largest of these, between S_{11} and B_{11}(Cr), had the value -0.70. The correlation coefficient of greatest magnitude among the S_{ij} themselves was -0.49, between S_{33} and S_{23}. Thus the form of anisotropic scale factor adopted here behaves reasonably well under least-squares refinement.

Final values of the atomic parameters are displayed in Table II. A listing of the observed and calculated structure factor magnitudes is available.[46]

Results and Discussion

The reaction of chromic acid with an excess of 2-hydroxy-2-methylbutyric acid in aqueous solution in the presence of mineral acid leads to the oxidation of the substrate to methyl ethyl ketone and carbon dioxide, and to the formation of initially equimolar quantities of chromium(V) and chromium(III).[33] Chromium(V) undergoes further reduction to chromium(III), first slowly and later very rapidly. Best yields of the chromium(V) product can be obtained when the reaction is carried out at low temperatures.
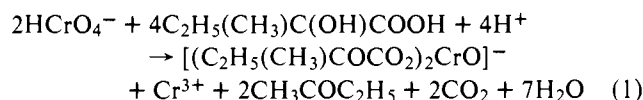
The product prepared by the procedure described in the Experimental Section has a molecular formula $C_{10}H_{18}CrKO_8$,

**Table I.** Experimental Data for the X-Ray Diffraction Study of $K[OCr(O_2CCOMeEt)_2]\cdot H_2O$

A. Crystal Parameters at 22 ± 1 °C[a]

$a = 12.362$ (6) Å
$b = 16.665$ (9) Å
$c = 7.611$ (3) Å
$\cos \beta = -0.0058$ (6)
$\beta = 90.33$ (3)°
$V = 1567.9$ (13) Å^3

Space group: Cc (no. 9, C_S^4)[b]
$Z = 4$
Mol wt = 357.35
ρ(calcd) = 1.514 g cm^{-3}
ρ(obsd)[c] = 1.518 (5) g cm^{-3}

B. Measurement of Intensity Data

Radiation: Mo Kα
Filter(s): Nb foil at counter aperture (47% transmission of Mo Kα)
Attenuators: not used, I(max) < 5000 counts/s
Take-off angle: 3.0°
Detector aperture: 6.3 × 6.3 mm
Crystal–detector distance: 330 mm
Crystal orientation: ϕ axis = 2.40° from $00l$, in $0kl$ plane
Reflections measured: $\pm h + k + l, h + k = 2n$; except that for $l = 0, h \geqslant 0$
Maximum 2θ: 40°
Scan type: coupled θ (crystal)–2θ (counter)
Scan speed: 2°(2θ)/min
Scan length: $\Delta(2\theta) = (1.60 + 0.692 \tan \theta)$°, starting 0.80° below the Mo Kα_1 peak.
Background measurement: stationary crystal, stationary counter; 20 s each at beginning and end of 2θ scan
Standard reflections: three remeasured after every 47 reflections; root mean square deviations (after application of an anisotropic linear decay correction)[d] were 0.44% for 200; 1.71% for 060; 0.91% for 002.
Reflections collected: 736 independent measurements and 34 systematic absences

C. Treatment of Intensity Data

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 39, using an "ignorance factor" of $p = 0.04$
Absorption coefficient: $\mu = 10.05$ cm^{-1}; maximum and minimum transmission factors were hand calculated[e] to be 0.928 and 0.901, respectively. No absorption correction was applied to the data.

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[a] Unit cell parameters are the averages of the results of two least-squares fits to the setting angles of the unresolved Mo Kα peaks (λ (av) = 0.71073 Å) of 12 and 7 (separate sets of measurements) reflections in the range $2\theta = 19$–35°. Individual parameter values differed by at most 1.3 times their estimated standard deviations. Root mean square setting angle disagreements were 0.046 and 0.038°, respectively. [b] "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1965, p 89. [c] The density was measured by neutral buoyancy in a carbon tetrachloride–hexane mixture. [d] Data reduction, including decay correction, was performed using the Fortran IV program RDUS2, by B. G. DeBoer. No standard reflection decayed by more than 9% of its initial intensity. [e] The crystal was a prism, 0.28 mm long, bounded by [110] faces which were separated by 0.086 and 0.090 mm.

which indicates that each atom of chromium is coordinated with two molecules of the hydroxy acid acting as a bidentate ligand, and the complex contains a potassium cation. The stoichiometry of the reaction is best expressed by

$$2HCrO_4^- + 4C_2H_5(CH_3)C(OH)COOH + 4H^+$$
$$\rightarrow [(C_2H_5(CH_3)COCO_2)_2CrO]^-$$
$$+ Cr^{3+} + 2CH_3COC_2H_5 + 2CO_2 + 7H_2O \quad (1)$$

The product is converted to the potassium salt during the workup procedure which includes neutralization with potassium hydrogen carbonate.
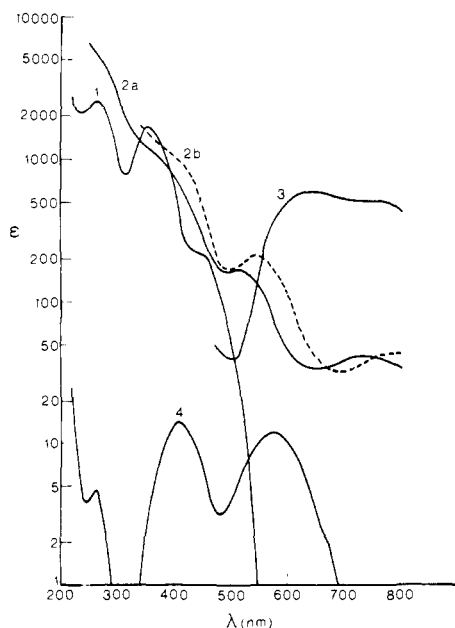
Figure 1. Electronic spectra of chromium(VI), chromium(V), chromium(IV), and chromium(III): (1) $HCrO_4^-$ in water, (2a) potassium bis(2-hydroxy-2-methylbutyrato)oxochromate(V) in 0.1 M 2-hydroxy-2-methylbutyric acid (aqueous solution), (2b) potassium bis(2-hydroxy-2-methylbutyrato)oxochromate(V) in acetone, (3) tetra(*tert*-butoxy)chromium(IV)[47] in dioxane, (4) hexaaquochromium(III) perchlorate in water.

The oxidation state of chromium was established from analytical studies, ultraviolet and electron spin resonance spectra, and magnetic measurements.

A relatively simple but reliable confirmation of the valence state of chromium was obtained iodometrically. Equal volumes of a solution of the chromium(V) complex were analyzed by standard iodometric titration: (a) directly and (b) after oxidizing all chromium to chromium(VI) by hydrogen peroxide in alkaline solution. $Na_2S_2O_3$ (6.68 mL, 0.01 M) was consumed to titrate a sample containing 0.0119 g (0.0334 mmol) of the chromium(V) complex by direct analysis, while 10.1 mL was required for the same amount after its oxidation to chromium(VI). This corresponds to a 1:1.51 ratio for (a):(b), which is in excellent agreement with the theoretical ratio of 1:1.50 for pentavalent chromium.

Another sample was analyzed by the recently developed iodometric method[33] by which chromium(V) and chromium(VI) can be determined separately owing to the ability of chromium(V) to oxidize iodide ions rapidly and quantitatively at much lower acidities. The results of this analysis (found: 14.3 Cr(V), 0.0 Cr(VI)) are also in very good agreement with the theoretical value (calcd 14.5 Cr(V), 0.0 Cr(VI)).

Figure 1 gives the ultraviolet and visible spectra of the chromium(V) salt in water and acetone. For comparison, spectra of chromium(VI), chromium(IV),[47] and chromium(III) are included. The most characteristic part of the chromium(V) spectrum is the broad, weak band observable in the 600–800-nm region (Figure 1, 2a) with a maximum at 733 nm (ϵ 41.8) and a minimum at 646 nm (ϵ 34.3). The only other maximum, observable at 510 nm (ϵ 170), is very shallow (minimum at 491 nm, ϵ 164) and is found in the region where both chromium(VI) and chromium(III) will interfere. At 350 nm, the wavelength usually used for monitoring chromium(VI), chromium(V) is a strongly absorbing species (ϵ 1220). This fact must be considered in all kinetic studies whenever a detectable amount of chromium(V) is formed, and a correction in handling the rate plots must be introduced.[33]

The absorption spectrum of the pure compound is in excel-

Table II. Final Positional and Thermal Parameters (with Esd's)[a] for $K[OCr(O_2CCOMeEt)_2]\cdot H_2O$

Atom	x	y	z	B, Å^2
Cr	0.25[b]	0.21556 (15)	0.50[b]	3.66[c]
K	−0.0595 (3)	0.06709 (19)	0.03339 (7)	3.61
O(1)	0.3371 (10)	0.1763 (8)	0.3814 (19)	6.0 (3)
O(2)	0.1382 (8)	0.1355 (6)	0.4998 (15)	3.4 (2)
C(1)	0.1241 (14)	0.0980 (10)	0.6461 (24)	3.6 (4)
O(3)	0.0548 (9)	0.0463 (7)	0.6608 (16)	3.9 (2)
C(2)	0.2039 (13)	0.1189 (10)	0.7861 (26)	4.4 (4)
O(4)	0.2665 (9)	0.1873 (7)	0.7222 (16)	4.2 (2)
C(3)	0.1555 (19)	0.1385 (15)	0.9469 (33)	7.9 (6)
C(4)	0.0789 (18)	0.2029 (12)	0.9306 (33)	7.7 (6)
C(5)	0.2871 (15)	0.0460 (12)	0.8132 (28)	6.2 (5)
O(5)	0.3178 (9)	0.3133 (6)	0.5679 (16)	3.9 (2)
C(6)	0.2828 (12)	0.3756 (9)	0.4879 (23)	3.2 (3)
O(6)	0.3259 (9)	0.4441 (7)	0.5034 (16)	4.6 (3)
C(7)	0.1871 (14)	0.3635 (11)	0.3693 (27)	4.4 (4)
O(7)	0.1553 (8)	0.2808 (6)	0.3919 (14)	3.5 (2)
C(8)	0.0960 (17)	0.4158 (12)	0.4246 (28)	6.0 (5)
C(9)	0.0599 (19)	0.4016 (14)	0.6038 (32)	7.8 (6)
C(10)	0.2195 (17)	0.3750 (13)	0.1738 (30)	7.4 (6)
W	0.4253 (10)	0.2748 (7)	0.9253 (17)	5.6 (3)

[a] Estimated standard deviations (esd's) are shown in parentheses and are right-adjusted to the last digit of the preceding number. They are calculated from the inverse of the least-squares matrix formed in the last cycle of refinement. [b] These (arbitrary) values were fixed in order to define the origin of coordinates in the x and z directions. [c] The chromium and potassium atoms were permitted anisotropic thermal parameters which enter the structure factor equation in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. Final values of these parameters (in the order in which they appear above) were 3.40 (15), 3.13 (15), 4.46 (18), −0.48 (12), 0.50 (13), 0.54 (14) for chromium and 3.51 (19), 2.90 (18), 4.42 (24), 0.23 (15), 0.27 (17), −0.57 (17) for potassium. The values appearing in the table are the so-called "equivalent" isotropic parameters.

lent agreement with that constructed earlier from measurements of aqueous solutions containing chromium(V) along with chromium(III) and other components present in the course of chromic acid oxidation of 2-hydroxy-2-methylbutyric acid.[32] It is also consistent with other chromium(V) spectra constructed indirectly from a computer analysis of the kinetic data by Wiberg and Lepse[48] (in 250–550-nm region), and by Srinivasan and Roček[30] (in 400–600-nm region).

The ESR spectrum of an aqueous solution of the chromium(V) compound at room temperature consists of a sharp single line at $g = 1.9780 \pm 0.0005$ ($I = 0$ for ^{52}Cr) accompanied by a four-component hyperfine structure due to the ^{53}Cr isotope ($I = 3/2$) with a natural abundance of 9.55%. This is in full agreement with data published by Kon.[8,9] Similar g values have been reported by Garifyanov for chromium(V) solutions obtained by chromium(VI) oxidation of glycerol[10] ($g = 1.975$) and ethylene glycol[11] ($g = 1.975$). Wiberg and Schafer[49] observed a well-defined signal ($g = 1.9805$) growing and decaying in the course of chromic acid oxidation of isopropyl alcohol in 97% acetic acid. As the ESR signal of chromium(III) consists of a very broad singlet[50] and chromium(IV) produces an ESR signal only at very low temperatures,[51] our findings confirm that the signal we observed at $g = 1.9780$ is due to the presence of chromium(V), a paramagnetic ion with d^1 electron configuration.[52]

The presence of one unpaired electron was also confirmed by magnetic measurements on the Gouy balance. An aqueous solution of the chromium(V) salt was used and the molar susceptibility ($\chi_M = 1760 \times 10^{-6}$ cm^3 M^{-1}, 25 °C) and the magnetic moment ($\mu_{calcd} = 1.73$ μ_B, $\mu_{eff} = 2.05$ μ_B) determined. These values are in good agreement with data obtained

by Krauss[20] for $CrOCl_3$ (μ_{eff} = 1.80 μ_B) and for $K_2[CrOCl_5]$ (μ_{eff} = 1.92 μ_B).

The infrared spectrum shows the presence of a carbonyl band at 1683 cm^{-1} (s). The lowering of the antisymmetric COO stretching frequency which in 2-hydroxy-2-methylbutyric acid appears at 1725 cm$^-$ (s) is consistent with the formation of a metal-oxygen bond and has been reported, e.g., for metal-glycolato complexes with cyclic structure[53] or other metal-chelate complexes with oxygen donors.[54] The shift in the stretching frequency, which depends on the metal,[53] indicates that a carboxyl group is coordinated to a chromium(V) ion. Terminal chromium-oxygen multiple bonds can be observed in the region below 1050 cm^{-1}. The sharp band at 994 cm^{-1} (s) (and possibly at 830 cm^{-1} (m)) corresponds to $\nu(Cr{=}O)$ vibrations; similar assignments have been made for a number of chromates and dichromates studied by Miller and Wilkins,[55] for halooxo complexes of pentavalent chromium,[23] and for peroxychromium compounds.[19] The absence of bands characteristic of un-ionized carboxyl and hydroxyl groups (a very weak absorption observed at 3250-3450 cm^{-1} would indicate the presence of lattice water) and the results of the elemental analysis suggest that the chromium(V) complex has a bicyclic structure and that bonding between the central atom and the ligands occurs through carboxyl and hydroxyl oxygens. Similar bicyclic structures have been considered on the basis of ESR data for chromium(V) complexes formed in the photochemical or thermal reduction of chromium(VI) by polyols[11-15] or by aqueous oxalic acid.[30]

All the results discussed above as well as those of the x-ray analysis are consistent with the following structure:
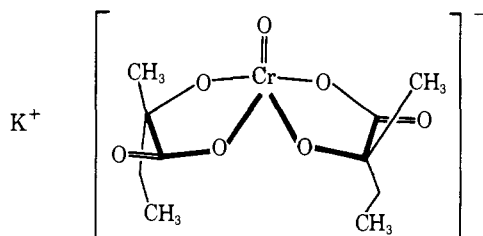

It has been frequently assumed that chromium(V) should be tetracoordinated and it was proposed[56] that the slow reduction of chromium(V) to chromium(IV) can be associated with the extensive rearrangement which must be accomplished in reducing a tetracoordinated chromium(V) to hexacoordinated chromium(IV). This assumption is not supported by our results and the unusual stability of this complex makes the above interpretation less attractive. The observation that chromium(V) forms quite stable pentacoordinated compounds strengthens our earlier expressed belief[57] that the relatively low reactivity of chromium(V) as compared with chromium(IV) could be better understood in terms of differences in reduction potentials of these two valence states.

Potassium bis(2-hydroxy-2-methylbutyrato)oxochromate(V) monohydrate is very stable at room temperature. It can be exposed to air and light for several weeks without obvious decomposition. The solid does not show a melting point but slowly decomposes around 130 °C. It is readily soluble in water, acetone, pyridine, dimethylformamide, dimethyl sulfoxide, acetic acid, acetic anhydride, and liquid ammonia, somewhat less soluble in methyl acetate and tetrahydrofuran, and insoluble in chloroform, carbon tetrachloride, diethyl ether, and both aliphatic and aromatic hydrocarbons.

The stability of aqueous solutions increases with the concentration of the compound: while dilute solutions (5 $\times$ 10^{-4} M) are decomposed within a few hours at room temperature, about 1 day is required for the decomposition of 0.01 M solutions. The stability of dilute solutions can be substantially increased by the addition of a small amount of 2-hydroxy-2-

methylbutyric acid, suggesting that the decomposition is preceded by a reversible hydrolysis. Acetone solutions show no observable decomposition over a period of several days at room temperature. The chromium(V) compound is also soluble in primary and secondary alcohols (methanol, ethanol, propanol, isopropyl alcohol) and polyols (ethylene glycol, glycerol). The stability of these solutions is comparable to that of aqueous solutions.

Addition of base, e.g., a dilute sodium hydroxide solution, to an aqueous solution of the chromium(V) compound leads to immediate quantitative disproportionation to chromium(VI) and chromium(II):

$$3Cr(V) \rightarrow 2Cr(VI) + Cr(III) \qquad (2)$$
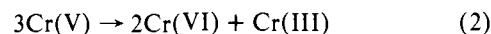
The aqueous solution of the complex also undergoes disproportionation upon acidification. However, the disproportionation in acidic solution is accompanied by some oxidation of the hydroxy acid either by chromium(V) itself or by the chromium(IV) intermediate. Consequently, the amount of chromium(VI) obtained in acid disproportionation is always lower (by about 60-65%) than would correspond to eq 2.

An aqueous solution of the free acid was obtained by passing a solution of the potassium salt of the chromium(V) complex through a cation-exchange resin in the hydrogen ion form (Dowex 50-X8, 50-100 mesh). The free acid is less stable than its potassium salt and attempts to isolate it have failed. The UV-visible spectrum of the acid is identical with that of the salt. Potentiometric measurements indicate that the acid is very strong and appears fully ionized (pH 2.1 at 0.01 M and 25 °C).

The astonishing stability of the bis(2-hydroxy-2-methylbutyrato)oxochromate(V) anion even in aqueous solutions must be due to two factors. First, the hydroxy acid anion obviously represents an exceptionally good chelating ligand which forms a strong complex with chromium(V).

Second, the chromium(V) complex possesses quite unusual and unexpected stability toward oxidative decomposition. This is particularly surprising in the light of the fact that many oxidations of α-dihydroxy compounds are believed to proceed by a cyclic mechanism (eq 3). A mechanism of this type is not
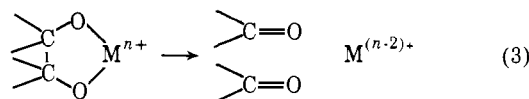
only assumed for the well-known lead tetraacetate and periodic acid oxidations but also for a number of other oxidants,[58] including chromium(VI).[59] The puzzling question with respect to the stability of potassium bis(2-hydroxy-2-methylbutyrato)oxochromate(V) is why this compound, which should be ideally preformed for an oxidative decomposition to carbon dioxide, a ketone, and a chromium(III) species by a cyclic two-electron process, in fact does not react. Since it seems obvious that the reaction should be accompanied by a favorable enthalpy and entropy change, it is likely that reaction 4 is
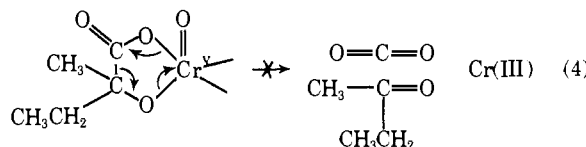
prevented by an unexpectedly high activation energy. The existence of such a high energy barrier for the thermal[60] pericyclic two-electron reduction of chromium(V) could suggest that this process may be symmetry forbidden.

Such an interpretation would seem consistent with the fact that most relatively stable chromium(V) compounds or intermediates have been formed in the presence of bidentate ligands like glycols[10-16] or oxalic acid.[30] The fact that both
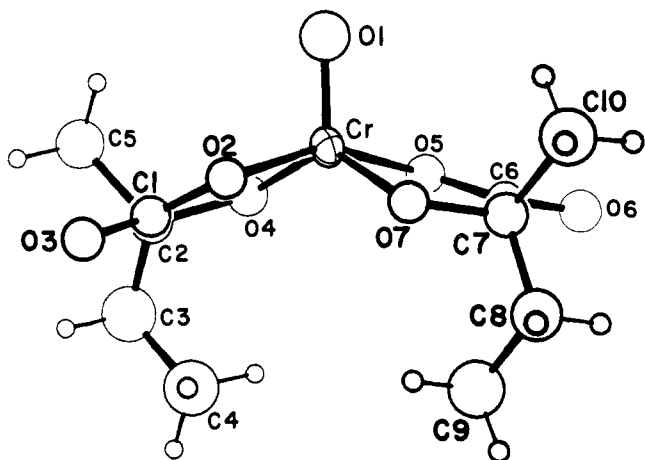
Figure 2. View of the bis(2-hydroxy-2-methylbutyrato)oxochromate(V) anion normal to Cr–O(1), illustrating the atom numbering (ORTEP diagram, 30% probability contours for nonhydrogen atoms).
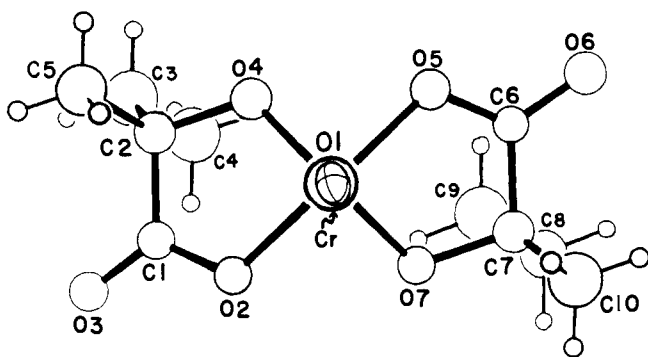

Figure 3. View of the [OCr(O₂CCOMeEt)₂]⁻ ion parallel to Cr–O(1), illustrating its virtual C_2 symmetry (drawn as for Figure 2).

Table III. Interatomic Distances (in Å, with Esd's)[a] for K[OCr(O₂CCOMeEt)₂]·H₂O

Atoms	Dist	Atoms	Dist
Cr–O(1)	1.554 (14)		
Cr–O(2)	1.921 (10)	Cr–O(4)	1.767 (12)
Cr–O(5)	1.902 (11)	Cr–O(7)	1.795 (10)
C(1)–O(2)	1.29 (2)	C(1)–O(3)	1.22 (2)
C(6)–O(5)	1.28 (2)	C(6)–O(6)	1.26 (2)
C(2)–O(4)	1.46 (2)	C(1)–C(2)	1.49 (2)
C(7)–O(7)	1.44 (2)	C(6)–C(7)	1.50 (2)
C(2)–C(3)	1.40 (3)	C(3)–C(4)	1.44 (3)
C(7)–C(8)	1.49 (3)	C(8)–C(9)	1.46 (3)
O(2)···O(7)	2.57 (2)	C(2)–C(5)	1.60 (2)
O(4)···O(5)	2.49 (2)	C(7)–C(10)	1.55 (3)
O(2)···O(4)	2.47 (2)	K···W[n][b]	2.731 (12)
O(5)···O(7)	2.47 (2)	K···O(2)	2.971 (11)
		K···O(3)	2.875 (12)
W···O(4)	2.89 (2)	K···O(5)[n]	3.215 (12)
W···O(7)[n][b]	3.00 (2)	K···O(6)[n]	2.886 (12)
W···O(2)[n]	3.08 (2)	K···O(3)[c]	2.706 (12)
W···O(5)	3.09 (2)	K···O(6)[C]	2.810 (12)

[a] Esd's, shown as in Table II, were calculated from the full positional covariance matrix from the final refinement cycle plus the contribution from uncertainties in cell parameters. No corrections have been applied for the systematic "shrinkage" errors resulting from the atoms' thermal motions. [b] Symbols in brackets denote the symmetry transformation which relates the position of the indicated atom to that listed for it in Table II. Atoms labeled [n] are in the same hydrogen-bonded chain as unlabeled atoms, while those labeled [c] or [C] are in adjacent chains.

1,2-diols and oxalic acid stabilize chromium(V) suggests that factors other than the electronegativity of the ligands are of principal importance.[61] The resistance of chromium(V) in cyclic complexes toward reduction by its ligands is further indicated by the very unusual kinetic behavior observed in the chromic acid oxidation of 2-hydroxy-2-methylbutyric acid.[32,33] The reaction proceeds in two stages. In the first chromium(VI) is reduced to a mixture of chromium(V) and chromium(III) and the reaction obeys good first-order kinetics. In contrast, reduction of chromium(V) to chromium(III) in the second phase exhibits kinetic behavior typical of a free-radical chain reaction, suggesting that chromium(V) is incapable of reacting as a two-electron oxidant toward the hydroxy acid and is therefore reduced in a series of one-electron transfer steps.

X-Ray Diffraction. Interatomic distances and angles, together with their estimated standard deviations, are collected in Tables III and IV, respectively. Information derived by the least-squares fitting of planes to the atomic positions is presented in Table V.

Structure of the [OCr(O₂CCOMeEt)₂]⁻ Anion. As is evident from Figures 2 and 3, the bis(2-hydroxy-2-methylbutrato)-oxochromate(V) monoanion closely approximates C_2 symmetry (not imposed by crystal symmetry). The two chelating ligands have corresponding atoms mutually trans and are of the same chirality. However, both enantiomers of the complete anion are present in the crystal (see below).

The chromium–oxygen bond distances fall into three chemically distinct sets: the doubly bonded chromium–O(1), 1.554 (14) Å; chromium to the hydroxyl-derived O(4) and O(7), average = 1.781 ± 0.020[62] Å; and chromium to the carboxyl-derived O(2) and O(5), average = 1.911 ± 0.015[62] Å. The shortness of the Cr–O(1) distance confirms the pres-

ence of the expected double bond and may be compared to values in the range 1.56–1.62 Å found in a large number of chromate(VI) compounds[63] and in a series of oxobis (peroxo) (nitrogen ligand) chromium(VI) complexes.[64]

To our knowledge, an x-ray structure determination of only one other Cr(V) compound,[65] K₃[Cr(O₂)₄], has been reported. The dissimilar ligands preclude direct comparison with the present compound, but fruitful comparisons may be made with derivatives of the isoelectronic VO²⁺ ion. Comparison of bond distances found[66] for bischelate oxovanadium(IV) complexes of O₂CC(O)(C₆H₅)₂²⁻ and dl-tartrate reveals that the Cr–O(1) distance is 0.030 (18) Å and 0.065 (16) Å shorter than the corresponding V=O distances [1.584 (11) and 1.619 (7) Å, respectively]. Chromium to hydroxyl-derived oxygen distances are 0.105 (13) to 0.166 (14) Å shorter [range = 1.900 (8)–1.933 (8) Å] and those to carboxyl-derived oxygens are 0.049 (13) to 0.102 (13) Å shorter [range = 1.970 (9)–2.004 (6) Å]. These differences presumably reflect the smaller bonding radius expected of a formal Cr⁵⁺ as compared to a formal V⁴⁺ (*differences* in the effect of thermal motion upon these distances are expected to be small). Angles listed in the same place deviate from those found here by only a few degrees, and further confirm the great similarity of CrO³⁺ and VO²⁺.

In view of the relatively low quality of the intensity data (and the effects of thermal motion), chemically equivalent pairs of distances and angles, including those in the organic ligand, are not regarded as being significantly different from one another (or from "standard" values).

Even if we ignore the differing Cr–O distances, the distribution of the five-coordinated oxygen atoms about the chromium atom is neither square pyramidal nor trigonal bipyramidal, but intermediate between them. The most obvious deviation from square pyramidal geometry lies in the difference between the angles O(2)–Cr–O(5) = 155.6 (5)° and O(4)–Cr–O(7) = 132.3 (5)° (or equivalently, the two pairs of O(1)–Cr–O(x) angles). Each of these four oxygen atoms would have to be swung through an arc of approximately 6°

Table IV. Interatomic Angles (in Degrees)[a] for K[OCr(O₂CCOMeEt)₂]·H₂O

| Atoms	Angle	Atoms	Angle
O(1)-Cr-O(2)	102.0 (6)	O(1)-Cr-O(4)	111.5 (6)
O(1)-Cr-O(5)	102.3 (6)	O(1)-Cr-O(7)	116.2 (6)
O(2)-Cr-O(4)	84.0 (5)	O(2)-Cr-O(7)	87.3 (5)
O(5)-Cr-O(7)	83.8 (5)	O(4)-Cr-O(5)	85.4 (5)
O(2)-Cr-O(5)	155.6 (5)	Cr-O(2)-C(1)	115.9 (11)
O(4)-Cr-O(7)	132.3 (5)	Cr-O(5)-C(6)	114.7 (10)
O(2)-C(1)-O(3)	121.3 (16)	Cr-O(4)-C(2)	117.9 (10)
O(5)-C(6)-O(6)	123.2 (15)	Cr-O(7)-C(7)	117.1 (9)
O(2)-C(1)-C(2)	114.4 (16)	O(4)-C(2)-C(1)	107.1 (15)
O(5)-C(6)-C(7)	116.3 (14)	O(7)-C(7)-C(6)	105.7 (14)
O(3)-C(1)-C(2)	124.1 (16)	O(4)-C(2)-C(5)	107.0 (12)
O(6)-C(6)-C(7)	120.6 (15)	O(7)-C(7)-C(10)	107.6 (15)
C(1)-C(2)-C(5)	109.7 (15)	O(4)-C(2)-C(3)	109.7 (17)
C(6)-C(7)-C(10)	110.7 (16)	O(7)-C(7)-C(8)	108.6 (14)
C(1)-C(2)-C(3)	113.2 (16)	O(3)···K···O(6)[n][b]	169.4 (3)
C(6)-C(7)-C(8)	110.4 (15)	O(3)···K···W[n]	86.0 (4)
		O(3)···K···O(3)[c]	94.7 (3)
C(2)-C(3)-C(4)	112.5 (21)	O(3)···K···O(6)[C]	76.2 (3)
C(7)-C(8)-C(9)	114.0 (19)	O(6)[n]···K···W[n]	104.5 (4)
		O(6)[n]···K···O(3)[c]	77.6 (3)
O(4)···W···O(7)	116.1 (5)	O(6)[n]···K···O(6)[C]	96.1 (3)
O(4)···W···K	113.5 (5)	W[n]···K···O(3)[c]	146.5 (4)
O(7)···W···K	102.1 (4)	W[n]···K···O(6)[C]	123.5 (4)
		O(3)[c]···K···O(6)[C]	88.9 (3)
W···O(4)···Cr	116.9 (6)	O(2)···K···O(3)	43.9 (3)
W···O(4)···C(2)	125.1 (10)	O(2)···K···O(6)[n]	142.5 (4)
W···O(7)···Cr	112.9 (5)	O(2)···K···W[n]	65.1 (3)
W···O(7)···C(7)	124.3 (9)	O(2)···K···O(3)[c]	92.6 (3)
		O(2)···K···O(6)[C]	120.0 (4)

[a] See footnote *a*, Table III. [b] See footnote *b*, Table III.

Table V. Least-Squares Planes,[a] Deviations Therefrom, and Dihedral Angles in the [OCr(O₂CCOMeEt)₂]⁻ Ion

Atom	Dev, Å	Atom	Dev, Å
Plane I: $0.6673X - 0.6779Y - 0.3085Z = -1.585$			
Cr*	0.023 (1)	O(3)	−0.057 (12)
O(2)*	0.006 (11)	O(1)	1.468 (13)
C(1)*	−0.035 (17)	O(5)	−0.683 (12)
C(2)*	0.055 (18)	O(7)	−1.238 (10)
O(4)*	−0.049 (12)		
Plane II: $0.5886X - 0.1421Y - 0.7958Z = -1.816$			
Cr*	0.083 (1)	O(6)	0.074 (12)
O(5)*	−0.068 (12)	O(1)	1.531 (13)
C(6)*	0.017 (16)	O(2)	−0.539 (11)
C(7)*	0.070 (18)	O(4)	−1.081 (12)
O(7)*	−0.103 (10)		
Plane III: $0.4120X - 0.4474Y + 0.7938 Z = 2.696$			
Cr*	−0.019 (1)	O(5)*	0.007 (12)
O(1)*	0.004 (13)	O(4)	1.615 (12)
O(2)*	0.007 (11)	O(7)	−1.639 (10)
Plane IV: $0.6087X + 0.7784Y + 0.1534Z = 5.256$			
Cr*	−0.008 (1)	O(7)*	0.003 (10)
O(1)*	0.003 (13)	O(2)	−1.888 (11)
O(4)*	0.003 (12)	O(5)	1.848 (12)
Angle (I-II) = 137.3°			
Angle (III-IV) = 88.6°			

[a] Equations of planes are expressed in the orthonormal (Å) coordinate system given by $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$. Atoms marked by an asterisk were assigned unit weight; all others were given zero weight.

to achieve a square pyramidal set of central angles. Consideration of the same set of angles reveals that O(2) and O(5) would have to be swung through approximately 12° of arc (in the opposite direction) to become "axial" and O(5) and O(7) by ca. 6° each to become "equatorial" in a trigonal bipyramidal
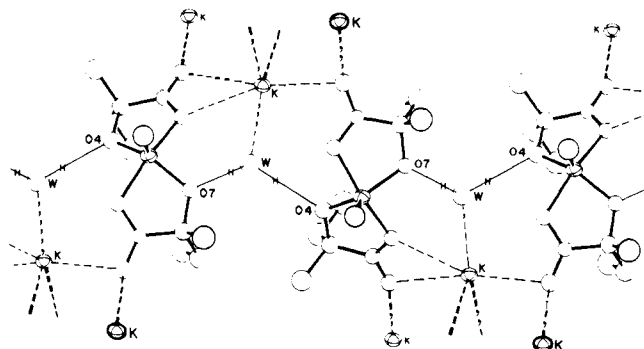
Figure 4. Three "links" in the hydrogen-bonded chain of anions parallel to [101], viewed perpendicular to [010]. Dashed lines indicate all potassium ion contacts shorter than 3.0 Å (drawn as for Figure 2).

central geometry (plus a small adjustment to bring equatorial and axial directions to the perpendicular).

As Table V illustrates, the five-membered chelate rings are neither strictly planar or coplanar with the carboxyl groups. However, the degree of puckering is not severe, is distributed differently in the two rings, and is undoubtedly affected by the various sorts of "crystal packing" forces. Therefore, it would seem that no great errors are incurred if they are thought of as planar while contemplating the chemistry of this ion.

The nearest neighbors of the unique oxygen, O(1), which are not part of the same anion, are various methyl and ethyl group hydrogen atoms, none closer than 3.1 Å. The sixth coordinating position of the chromium atom, opposite O(1), seems to be well guarded by the two ethyl groups in the conformation found here. A hand calculation gives Cr-C(4) = 3.92 Å, Cr-C(9) = 3.97 Å, and C(4)-C(9) = 4.15 Å, or approximately van der Waals distances. Of course, in solution the ethyl groups could swing away, permitting one to consider six-coordinate species.

One can envisage six geometric (ten optical) isomers for $[OCr(O_2CCOMeEt)_2]^-$. Three enantiomeric pairs are of the trans configuration about the chromium atom and one enantiomeric pair plus two "meso" isomers are of the cis configuration. The trans configuration is favored over the cis by its antiparallel arrangement of the dipole moments within the two organic ligands, but it is not clear which configuration would be favored by other factors (such as "trans" bonding effects in the chromium coordination). The relative dispositions ("up" or "down") of the methyl and ethyl groups could be affected by more subtle influences, including the stabilities and rates of formation of the crystalline solids.

Structure of the Crystal. The crystals of potassium bis(2-hydroxy-2-methylbutyrato)oxochromate(V) monohydrate consist of an ordered racemic array of anions, bound into infinite chains (ignoring the finite extent of any particular crystal) by intervening hydrogen-bonded water molecules and by potassium cations as shown in Figure 4. Successive "links" in these chains are related by the crystallographic n-glide symmetry operation. This requires that each $[OCr(O_2CCOMeEt)_2]^-$ ion is the enantiomer of its neighbors in the chain. The chains extend in the crystallographic $(a + c)$ direction and adjacent chains are cross-linked through the potassium cations.

Potassium ions are coordinated by five groups: a water molecule and two carboxyl groups in the same chain, and two additional carboxyl groups in each of two other chains. This coordination polyhedron has, at best, C_2 symmetry, and that only very approximately. Details are given in Tables III and IV.

The hydrogen-bonding pattern of the water molecule, described above and illustrated in Figure 4, is inferred on the grounds of geometrical reasonableness. This hydrogen-bond placement is the only one which yields reasonable hydrogen-bonded O···O distances and a reasonable H–O–H angle, and directs the negative end of the water dipole toward the nearby potassium ion.

Supplementary Material Available: A list of the observed and calculated structure factors and the hydrogen atom parameters (3 pages). Ordering information is given on any current masthead page.
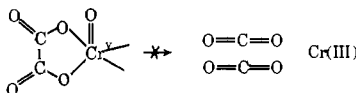
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(1) Support for this investigation by a grant from the National Science Foundation is gratefully acknowledged.
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The Molybdenum–Molybdenum Triple Bond. 3. A Triple Bond between Two Four-Coordinated Molybdenum(III) Atoms. Structural Characterization of the Bis(dimethylamine) Adduct of Dimolybdenum Hexatrimethylsiloxide

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Abstract: The crystal and molecular structures of the compound $Mo_2(OSiMe_3)_6 \cdot 2NHMe_2$ are reported. The molecule has a nonbridged structure, $(Me_3SiO)_3(Me_2HN)MoMo(Me_2HN)(OSiMe_3)_3$, with an Mo–Mo distance of 2.242 (1) Å, a mean Mo–O distance (average of six) of 1.95 ± 0.02 Å, and a mean Mo–N distance (average of two) of 2.282 ± 0.004 Å. The rotational conformation is intermediate between eclipsed and staggered, but closer to the latter. The compound crystallizes in the space group $C2/c$ with unit cell dimensions of $a = 40.016$ (5), $b = 11.497$ (1), $c = 18.829$ (2) Å, $\beta = 98.65$ (1)°, and $V = 8564$ (2) Å³. The structure was solved and refined to $R_1 = 0.056$ and $R_2 = 0.085$ using 3529 independent reflections having $I > 3\sigma(I)$. This compound is thus shown to provide the first proven example of a molecule containing two four-coordinate metal atoms triply bonded to each other, without any bridging groups, that is obtained by the reversible addition of two ligands to a triply bonded M_2X_6 molecule. The Mo–Mo distance is only slightly longer than that in the alkoxide $Mo_2(OCH_2CMe_3)_6$, 2.222 Å, but considerably longer than typical Mo–Mo quadruple bonds, 2.09–2.15 Å.

Introduction

In the now well-established chemistry of transition metal compounds containing multiple bonds between metal atoms,[2] especially triple and quadruple bonds, the most common structural pattern[3] is such that with quadruple bonds each metal atom is four coordinated while with triple bonds, the metal atoms are three coordinated. Thus, in the former case, the most typical sorts of species have been $X_4M\text{-}MX_4^{n-}$, $M_2(O_2CR)_4$, $M_2(SO_4)_4^{n-}$, or $M_2(O_2CR)_4L_2$, while in the case of triple bonds the predominant structure type has been $L_3M\text{-}ML_3$. There are, of course, exceptions to the above generalizations. Those pertinent to this discussion are cases in which a triple bond exists between metal atoms each bonded to four ligand atoms.

The first such case, $Re_2Cl_5(MeSCH_2CH_2SMe)_2$ (I), was reported as long ago as 1966[4] (and actually constitutes the first reported example of *any* triple bond between transition metal atoms). The rotational configuration here is staggered, as expected when there is no δ bond to favor the eclipsed configuration. Very recently the situation represented schematically in II has been found to occur[5] in the compound $La_4(Re_2)O_{10}$; in this case the configuration is eclipsed (overall symmetry D_{4h}) because this arrangement is imposed by the crystal
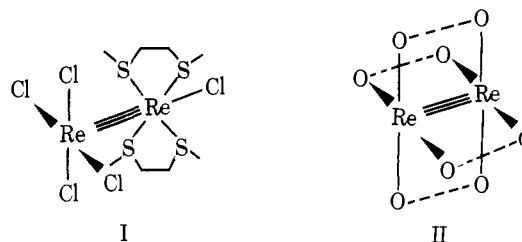
structure in its entirety. In both of these cases, the Re–Re bonds are triple bonds in the simplest sense of that term, namely, in having three pairs of electrons involved primarily in metal–metal interaction and an electron configuration we can represent as $\sigma^2\pi^4$.

For tetrakis(2,6-dimethoxyphenyl)divanadium[6] a structure in which each of the two vanadium atoms, which are triply bonded to each other, is coordinated by two carbon atoms and two oxygen atoms has been suggested.[6] However, it has been found that this structure, though plausible, is incorrect. In fact, there is a V–V triple bond ($d_{V-V} = 2.198$ Å) but the arrangement of the ligands is more complicated.[7]

There are also the molecules of the type $Re_2X_4(PR_3)_4$[8,9] for which an SCF-Xα-SW calculation[10] indicates a $\sigma^2\pi^4\delta^2\delta^{*2}$

I   II