210° (measured from the side of the anion with the terminal sulfido ligands). All other distances and angles of **3** are identical with those of the syn conformer whose structure has been described above. No example of conformer **3** has yet been reported for binuclear Mo(V) complexes in which the Mo atoms are five-coordinate. For six-coordinate binuclear Mo centers conformer **3** becomes two distorted octahedra sharing a face. Three structures of such triply bridged binuclear Mo(V) complexes have been described.[29-31] The largest dihedral angle in such complexes is 196°.[29]

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Registry No. *syn*-$[TEA]_2[Mo_2S_4(dme)_2]$, 65137-01-1; *anti*-$[TEA]_2[Mo_2S_4(dme)_2]$, 65045-66-1.

Supplementary Material Available: Tables of distances and angles in the TEA cations and structure factor tables (24 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Tris[tetra-μ-formato-diaquodichromium(II)] Decahydrate: A Case of an Unusually Good False Minimum in a Structure Solution

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The title compound, $[Cr_2(O_2CH)_4(H_2O)_2]_3{\cdot}10H_2O$, crystallizes from a dilute aqueous solution of chromium(II) formate in the tetragonal space group $I4_1/acd$. The unit cell has the dimensions $a = 17.929$ (3) Å, $c = 25.198$ (3) Å, $V = 8100$ (4) Å^3, $d_x = 1.87$ g/cm^3, and $Z = 8$ for the formula given. The 48 chromium atoms in the unit cell are all present in $Cr_2(O_2CH)_4(H_2O)_2$ units and these are of two crystallographically independent types having Cr–Cr distances of 2.373 (2) and 2.360 (2) Å, while the respective Cr–O_{ax} distances are 2.268 (4) and 2.210 (6) Å. The structure initially refined to a false minimum ($R_1 = 0.0551$, $R_2 = 0.0805$), but this was recognized because of unreasonable values of some internuclear distances. A structure with reasonable values of these bond lengths and significantly lower residuals ($R_1 = 0.0505$, $R_2 = 0.0684$) was found to be stable under refinement and is reported in detail.

Introduction

Among the carboxylato complexes of both chromium(II) and copper(II), of the general formula $M(O_2CR)_2(L)_x$, the hydrated formato complexes $M(O_2CH)_2(H_2O)_x$ are remarkable for the range of values x may assume.[1,2] Both color and magnetic properties vary with x. At least four distinct hydrates have been reported for chromium(II) formate[1] and two for copper(II) formate,[2] in addition to the anhydrous metal

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formates.[2,3] The four hydrated chromous formates were reported[1] to have the following formulas, colors, and magnetic moments:

1	$Cr(O_2CH)_2 \cdot H_2O$	Red	1.35 μ_B
2	$Cr(O_2CH)_2 \cdot 2.5H_2O$	Red	0.52 μ_B
3	$Cr(O_2CH)_2 \cdot H_2O$	Red	0.59 μ_B
4	$Cr(O_2CH)_2 \cdot 0.5H_2O$	Violet	2.85 μ_B

As part of a general investigation of the influence of axial ligands upon chromium–chromium bonding in $Cr_2(O_2CR)_4(L_{axial})_2$ molecules, we have undertaken studies of the chromium(II) formate system. We have already reported[4] the structure of **1**, for which the correct formula is $Cr_3(O_2CH)_6(H_2O)_2$. We have now found that the most water-rich hydrate, **2**, to which the formula $Cr(O_2CH)_2(H_2O)_{2.5}$ was previously assigned,[1] actually has the stoichiometry $Cr(O_2CH)_2(H_2O)_{8/3}$. While **1** contains one-third of the chromium atoms as isolated, six-coordinate Cr^{2+} ions, compound **2** contains all chromium atoms in $Cr_2(O_2CH)_4$ units.

Experimental Section

Synthesis and Crystallization of $[Cr_2(O_2CH)_4(H_2O)_2]_3(H_2O)_{10}$. The compound was prepared according to the method described by Herzog and Kalies[1] for "$Cr(O_2CH)_2(H_2O)_{2.5}$". A sodium formate/formic acid solution was prepared from 20 mL of H_2O, 4 g (100 mmol) of NaOH, and 6 mL (140 mmol) of 90% HO_2CH. Addition of 4.5 g (17 mmol) of $CrCl_3 \cdot 6H_2O$ in 20 mL of dilute HCl through a Jones reductor column yielded a homogeneous purple solution. This was chilled slowly by suspending the flask above ice in a covered Dewar. The product formed as large, cubic crystals. These appeared to be purple in the massive state but were red when finely crushed or when viewed with transmitted light. The crystals were washed once with degassed water and covered with degassed mineral oil. Selected specimens were wedged into mineral-oil-filled capillaries.

X-Ray Data Collection. All data were collected at 22 ± 2 °C on a Syntex $P\bar{1}$ automated diffractometer using Mo Kα radiation with a graphite crystal monochromator in the incident beam. Centering and indexing of 15 intense reflections with $0° < 2\theta < 20°$ according to a routine procedure[5] yielded initially what appeared to be a body-centered cubic cell with $a = 12.6$ Å. Axial photographs, however, revealed weak but well-defined spots requiring axes of twice this length. Further attempts to center and index 15 reflections with $25° < 2\theta < 31°$ showed that the unit cell was tetragonal rather than cubic, and preliminary examination of an octant of data, $0° < 2\theta < 12°$, required the choice of a body-centered tetragonal cell with the following dimensions: $a = 17.929$ (3) Å, $c = 25.198$ (3) Å, $V = 8100$ (4) Å^3, and $d_x = 1.87$ g/cm^3 for $Z = 8$ for the compositional unit $[Cr_2(O_2CH)_4(H_2O)_2]_3 \cdot 10H_2O$ having a formula weight of 1140.46.

The data were taken with a crystal of dimensions 0.3 × 0.3 × 0.45 mm, which yielded ω scans of full width at half-height of 0.13–0.16°. A total of 2636 reflections with $0° < 2\theta \leq 55°$ were collected using the θ–2θ scan technique, variable scan rates from 4.0 to 24.0°/min, and a scan range from 2θ(Mo Kα_1) – 0.8° to 2θ(Mo Kα_2) + 0.8°. Intensities of 4 standard reflections measured after every 96 reflections showed no significant decay during data collection. Lorentz and polarization corrections were applied,[6] but an absorption correction was deemed unnecessary ($\mu = 17.4$ cm^{-1}).

Solution and Refinement of the Structure.[6] The space group $I4_1/acd$ (No. 142) was uniquely determined by the systematic absences. The presence of each glide plane was tested by over 100 reflections in the data collected. The structure was solved and refined in the second setting of the space group $I4_1/acd$, with the origin at $\bar{1}$. Rejection of systematically absent reflections from the data set left 2325 reflections, of which 1170 had $F_o^2 > 3\sigma(F_o^2)$ and were considered observed. During refinement of the model, the two most intense reflections, 004 and 220, were observed to have markedly disparate F_o and F_c due, presumably, to extinction, and these were omitted from the set of observations. Approximately 530 of the observed reflections defined the large, tetragonal cell and would be unobserved if the small cubic cell were correct.

The positions of the chromium atoms were found in an E map using as a starting phase set the one with the highest figure of merit produced by the program MULTAN. The remaining atoms were found by repeated alternation of full-matrix least-squares cycles and difference Fourier map computations. The structure was refined to convergence using anisotropic temperature factors for all atoms, yielding discrepancy indices

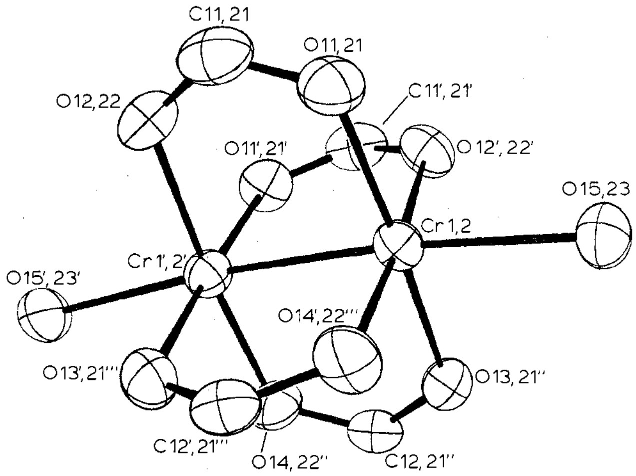

Figure 1. An ORTEP drawing of the $Cr_2(O_2CH)_4(H_2O)_2$ moiety containing Cr(1). Thermal ellipsoids enclose 50% of the electron density. For each atom, the first number designates an atom in the moiety containing Cr(1) while the second number designates an atom in the molecule containing Cr(2). Singly primed atoms are generated from unprimed ones by twofold axes which bisect the Cr–Cr bonds at 45° to the planes of the OCO ligands. Doubly and triply primed atoms are generated by additional twofold axes in the Cr(2)-containing moiety.

$$R_1 = \Sigma ||F_o| - |F_c|| / |F_o| = 0.0551$$

$$R_2 = [\Sigma w(||F_o| - |F_c||)^2 / \Sigma w |F_o|^2]^{1/2} = 0.0805$$

The function minimized during all least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor w equals $4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for p in the calculation of σ.[6]

Although these residuals are marginally satisfactory, some of the calculated bond lengths were chemically unreasonable and there were some very different lengths for (presumably) chemically equivalent bonds. In particular, the Cr(2)–O(21) and Cr(2′)–O(22) bonds were 1.99 and 2.06 Å, the O(21)–C(21) and O(22)–C(21) bonds were 1.34 and 1.17 Å, and the O–C–O groups on Cr(1) possessed similar, though smaller, asymmetry. Since the choice of space group seemed to be unimpeachable, several disorder models were tested in an attempt to resolve the problem. When these failed, the following unusual step was taken: The positions of the five offending atoms, O(21), O(22), C(11), C(12), and C(21), were reset to produce reasonable bond distances. Refinement in three full-matrix least-squares cycles then led to convergence at a new minimum with discrepancy indices $R_1 = 0.0504$ and $R_2 = 0.0684$. These improvements of 0.0047 in R_1 and 0.0121 in R_2 were achieved with no change in either the number of parameters (133) or the number of observations (1168). Additionally, the greatest difference in the position of an atom in the two minima was 0.080 Å, while the average difference was 0.023 Å for the 16 atoms in the model.

In view of this behavior, several steps were taken to verify the quality of the crystal. Long-exposure Weissenberg and rotation photographs of the data crystal revealed no superstructure spots, diffuse scattering, or streaks suggestive of disorder. The optical quality of this and other crystals was good. No tendency toward gross twinning was detected optically in any of several batches of crystals grown. Centering and indexing reflections from two additional crystals gave, again, the cell constants reported here, and axial photographs from these crystals were similar to those obtained from the data crystal. Since three distinct absence conditions were obeyed perfectly, twinning of the crystals was rendered less probable. After much deliberation and numerous discussions with colleagues we think twinning is quite unlikely except possibly, but not probably, in the following way.[7] It is recognized that while one-third of the observed reflections require the large tetragonal cell reported, the remaining two-thirds of the reflections would be nonzero for a cubic cell with a volume one-eighth of that observed. This allows the mere possibility that the latter

Table I. Positional and Thermal Parameters[a, b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr(1)	0.29139 (5)	0.04990 (5)	0.13534 (4)	0.00182 (3)	0.00198 (3)	0.00099 (1)	−0.00010 (5)	−0.00003 (3)	0.00013 (4)
Cr(2)	0.0	0.25	0.07816 (5)	0.00215 (4)	0.00211 (4)	0.00099 (2)	0.00063 (8)	0.00	0.0
O(11)	0.3573 (2)	0.0045 (3)	0.0786 (2)	0.0023 (2)	0.0032 (2)	0.00124 (7)	0.0002 (3)	0.0006 (2)	−0.0002 (2)
O(12)	0.2731 (3)	−0.0844 (3)	0.0625 (2)	0.0033 (2)	0.0022 (1)	0.00121 (7)	0.0003 (3)	0.0006 (2)	−0.0006 (2)
O(13)	0.2208 (2)	0.0888 (2)	0.1911 (2)	0.0025 (1)	0.0026 (1)	0.00122 (7)	0.0002 (3)	−0.0001 (2)	−0.0008 (2)
O(14)	0.1341 (2)	0.0055 (3)	0.1696 (2)	0.0023 (1)	0.0029 (2)	0.00139 (7)	0.0000 (3)	0.0012 (2)	−0.0009 (2)
O(15)	0.3697 (3)	0.1448 (2)	0.1563 (2)	0.0027 (2)	0.0022 (2)	0.00184 (8)	−0.0007 (3)	−0.0006 (2)	−0.0004 (2)
O(21)	0.0023 (3)	0.1377 (3)	0.0809 (2)	0.0033 (2)	0.0020 (1)	0.00158 (8)	0.0005 (3)	−0.0008 (2)	−0.0004 (2)
O(22)	−0.0033 (3)	0.1371 (3)	0.1686 (2)	0.0035 (2)	0.0023 (2)	0.00148 (8)	0.0004 (3)	−0.0005 (2)	0.0006 (2)
O(23)	0.0	0.25	−0.0095 (3)	0.0030 (2)	0.0054 (3)	0.00117 (11)	0.0010 (5)	0.0	0.0
O(1)	0.0110 (3)	0.0747 (4)	−0.0315 (2)	0.0040 (2)	0.0057 (3)	0.00215 (11)	0.0024 (4)	−0.0011 (3)	−0.0004 (3)
O(2)	0.0140 (3)	0.1188 (3)	0.3149 (2)	0.0030 (2)	0.0031 (2)	0.00219 (9)	0.0009 (3)	0.0003 (2)	0.0014 (2)
O(3)	−0.0274 (4)	0.0	0.25	0.0029 (3)	0.0065 (4)	0.00194 (13)	0.0	0.0	−0.0017 (4)
C(11)	0.3346 (4)	−0.0519 (4)	0.0543 (3)	0.0034 (2)	0.0035 (3)	0.0009 (1)	0.0023 (4)	0.0007 (3)	0.0003 (3)
C(12)	0.1577 (4)	0.0602 (4)	0.1964 (3)	0.0021 (2)	0.0024 (2)	0.0012 (1)	0.0010 (4)	0.0003 (3)	0.0003 (3)
C(21)	−0.0005 (4)	0.1049 (4)	0.1246 (3)	0.0023 (2)	0.0023 (2)	0.0017 (1)	−0.0002 (4)	−0.0009 (3)	0.0007 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Figures in parentheses are esd's occurring in the least significant digits. Figures without esd's are those fixed by symmetry.

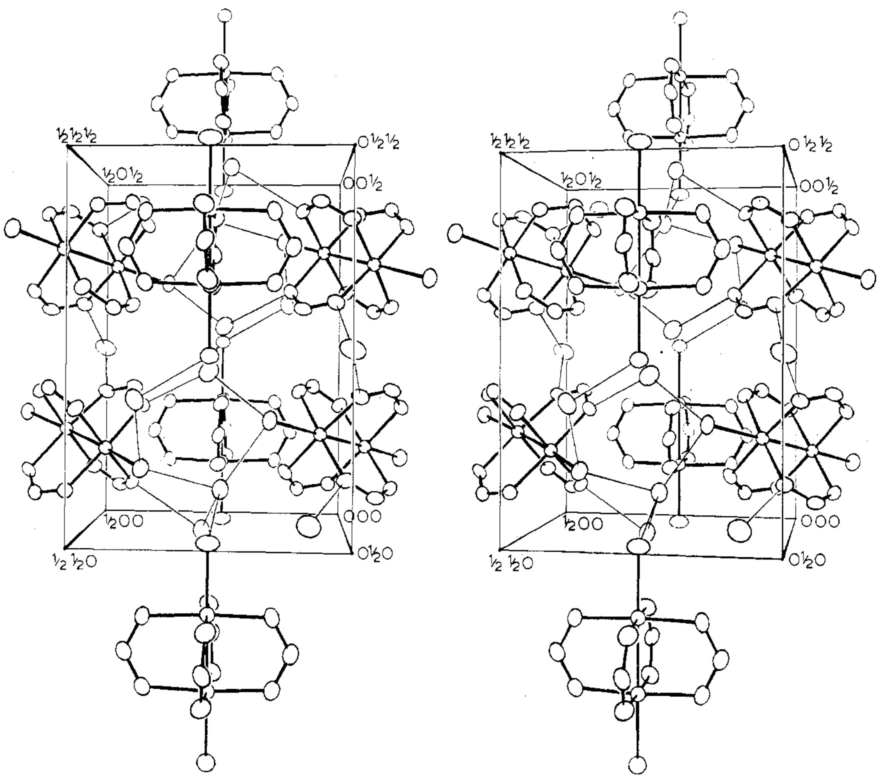

Figure 2. A stereographic projection of one-eighth of the unit cell on the xz plane using 30% thermal ellipsoids. Bonds within molecules are shown by heavy lines while presumed hydrogen bonds (O–O contacts less than 3.0 Å) are shown by light lines. The vertices are labeled in fractional coordinates and the inversion center at $^1/_4$, $^1/_4$, $^1/_4$ is represented by a dot. The dimer units parallel to the z axis are those containing Cr(2).

reflections, being rather more numerous and more intense than the former, could contain some form of pseudosymmetry which even a full-matrix least-squares refinement cannot break without intervention.

The error in an observation of unit weight was 1.378 for the better solution. A final difference Fourier map had as its largest peak one of 1.8 e/Å^3. The peaks in the map possessed no pattern indicative of disorder in the structure. Tables of observed and calculated structure factors are available.[8] In view of the unusual false-minimum problem observed for this structure, we have also included in the supplementary material a set of tables of positional and thermal parameters and observed and calculated structure factors clearly marked as being those from the false minimum.[7]

Results

The positional and thermal parameters are listed in Table I. The molecular structures of the $Cr_2(O_2CH)_4(H_2O)_2$ units and the atom numbering schemes for the two distinct dimers are illustrated in Figure 1. The unit cell contains 48 chromium atoms paired into 24 dimeric molecules. Of these, 16 equivalent dimers contain the chromium atom Cr(1) in 32 general positions, while a second set of 8 equivalent dimers contains the chromium atom Cr(2) in 16 special positions. As is typical of molecules containing $Cr_2(O_2CR)_4$ units, the dimers closely approach D_{4h} symmetry although this symmetry is not crystallographically imposed. The imposed symmetry consists of a twofold rotation for the "general" dimer, for which the center of the Cr(1)–Cr(1) bond lies upon the twofold axis given by (x, $^1/_4 + x$, $^1/_8$). The "special" dimer has 222 symmetry, with the center of the Cr(2)–Cr(2) bond upon the point at (0, $^1/_4$, $^1/_8$) where three twofold axes intersect. Since the Cr(2) and O(23) atoms lie upon a twofold axis, the Cr(2′)–Cr(2)–O(23) angle is required to be 180°. Figure 1 was drawn with the atoms of the Cr(1) molecule and therefore gives a

Table II. Interatomic Distances and Angles[a]

Distances, Å			
Cr(1)–Cr(1′)	2.373 (2)	Cr(2)–O(22′)	2.027 (5)
Cr(2)–Cr(2′)	2.360 (2)	Cr(2)–O(23)	2.210 (6)
Cr(1)–O(11)	2.026 (4)	O(11)–C(11)	1.252 (8)
Cr(1)–O(12′)	2.009 (4)	O(12)–C(11)	1.263 (8)
Cr(1)–O(13)	2.017 (4)	O(13)–C(12)	1.249 (7)
Cr(1)–O(14′)	2.006 (4)	O(14)–C(12)	1.264 (7)
Cr(1)–O(15)	2.268 (4)	O(21)–C(21)	1.250 (7)
Cr(2)–O(21)	2.014 (5)	O(22)–C(21)	1.251 (8)
Angles, Deg			
Cr(1′)–Cr(1)–O(11)	88.3 (1)	O(11)–Cr(1)–O(13)	175.9 (2)
Cr(1)–Cr(1′)–O(12)	87.6 (1)	O(12)–Cr(1′)–O(14)	175.4 (2)
Cr(1′)–Cr(1)–O(13)	87.6 (1)	O(11)–Cr(1)–O(12′)	88.7 (2)
Cr(1)–Cr(1′)–O(14)	88.1 (1)	O(11)–Cr(1)–O(14′)	89.7 (2)
Cr(1′)–Cr(1)–O(15)	174.6 (1)	O(12′)–Cr(1)–O(13)	90.6 (2)
Cr(2′)–Cr(2)–O(21)	88.0 (1)	O(13)–Cr(1)–O(14′)	90.8 (2)
Cr(2)–Cr(2′)–O(22)	87.7 (1)	O(21)–Cr(2)–O(21″)	176.1 (3)
Cr(2′)–Cr(2)–O(23)	180.0[b]	O(22)–Cr(2′)–O(22″)	175.3 (3)
O(11)–Cr(1)–O(15)	96.0 (2)	O(21)–Cr(2)–O(22′)	90.4 (2)
O(12′)–Cr(1)–O(15)	95.7 (2)	O(21)–Cr(2)–O(22‴)	89.4 (2)
O(13)–Cr(1)–O(15)	88.1 (2)	O(21)–Cr(2)–O(23)	92.0 (1)
O(14′)–Cr(1)–O(15)	88.7 (2)	O(22′)–Cr(2)–O(23)	92.3 (1)
Cr(1)–O(11)–C(11)	118.6 (4)	Cr(2)–O(21)–C(21)	120.0 (4)
Cr(1′)–O(12)–C(11)	119.9 (4)	Cr(2′)–O(22)–C(21)	119.8 (4)
Cr(1)–O(13)–C(12)	120.0 (4)	O(11)–C(11)–O(12)	125.3 (6)
Cr(1′)–O(14)–C(12)	119.8 (4)	O(13)–C(12)–O(14)	124.4 (6)
		O(21)–C(21)–O(22)	124.3 (5)
Parameters Involving Oxygen–Oxygen Contacts[c]			
Distances, Å			
O(11)–O(1)	2.926 (6)	O(15)–O(2)	2.823 (6)
O(12)–O(3)	2.966 (7)	O(23)–O(2)	2.746 (5)
O(15)–O(1)	2.729 (6)	O(2)–O(3)	2.787 (6)
O(15)–O(2)	2.727 (6)		
Angles, Deg			
Cr(1)–O(11)–O(1)	125.8 (2)	C(11)–O(11)–O(1)	114.4 (4)
Cr(1)–O(12)–O(3)	125.2 (2)	C(11)–O(12)–O(3)	114.8 (4)
Cr(1)–O(15)–O(1)	121.5 (2)	O(1)–O(15)–O(2)	104.9 (2)
Cr(1)–O(15)–O(2)	121.4 (2)	O(1)–O(15)–O(2)	91.4 (2)
Cr(1)–O(15)–O(2)	104.0 (2)	O(2)–O(15)–O(2)	108.7 (2)
Cr(2)–O(23)–O(2)	120.6 (2)	O(2)–O(23)–O(2)	118.9 (3)
O(15)–O(2)–O(15)	109.4 (2)	O(11)–O(1)–O(15)	120.7 (2)
O(15)–O(2)–O(23)	117.6 (2)	O(12)–O(3)–O(12)	66.6 (2)
O(15)–O(2)–O(23)	84.4 (2)	O(12)–O(3)–O(2)	115.2 (2)
O(15)–O(2)–O(3)	129.6 (2)	O(12)–O(3)–O(2)	91.0 (2)
O(15)–O(2)–O(3)	92.0 (2)	O(2)–O(3)–O(2)	149.2 (3)
O(23)–O(2)–O(3)	109.4 (2)		

[a] The numbering scheme is that shown in Figure 1. [b] Required by symmetry. [c] Because of the large number of symmetry operations, no attempt has been made to label these atoms specifically. The O–O distances reported are those drawn in Figure 2.

very slight distortion of the structure of the Cr(2) dimer.

The pertinent bond distances and angles are reported in Table II. The bond lengths are all reasonable, and chemically equivalent bonds have the same lengths with the exception of the Cr(1)–O(15) and the Cr(2)–O(23) bonds. By comparison with the chromium–axial ligand bond lengths in a number of other $Cr_2(O_2CR)_4$ complexes,[4] the Cr(1)–O(15) distance of 2.268 (4) Å is as expected, but the Cr(2)–O(23) distance of 2.210 (6) Å is surprisingly short. In view of the problem with an apparent false minimum described in the Experimental Section, vide supra, an attempt was made to reset the position of O(23) so as to give a Cr(2)–O(23) distance of 2.26 Å, but refinement shifted the atom back to its original position.

The data reported in Table II include those distances and angles which could reasonably be assigned to the hydrogen-bonding contacts which play a key role in the packing. Since the hydrogen atoms were not found, we have reported all distances and angles involving O–O vectors less than the arbitrary value of 3.0 Å. There is some question as to whether the vectors involving O(11) and O(12) reflect hydrogen bonding or simple van der Waals contacts, but there is little doubt that the remaining contacts are indeed hydrogen bonds.

A stereographic projection illustrating the molecular packing and the presumed hydrogen bonding is given in Figure 2. As the labels on the vertices indicate, the box of enclosure comprises one-eighth of the complete unit cell. Although the portion of the cell shown is that octant generated by vectors from the origin to $a = {}^1/_2$, $b = {}^1/_2$, and $c = {}^1/_2$, each of the other octants would have the identical projection if the viewpoint were correctly chosen. The atoms included in Figure 2 are all those which are actually within the octant plus those required to complete dimer units which are partially within the octant.

Discussion

All of our observations on this compound, with the empirical formula $Cr(O_2CH)_2(H_2O)_{8/3}$, indicate that it is the one formulated by Herzog and Kalies[1] as $Cr(O_2CH)_2(H_2O)_{2.5}$, the difference being only ${}^1/_6$ H_2O per chromium atom. We had previously shown that, of the two compounds reported by the same authors as $Cr(O_2CH)_2(H_2O)$, the one obtained by crystallization from a moderately concentrated chromium(II) formate solution is in fact $Cr_3(O_2CH)_6(H_2O)_2$ and contains one dimer and one isolated chromium atom in the unit cell.[4] The other compound to which the formula $Cr(O_2CH)_2(H_2O)$ was assigned,[4] produced by dehydration of "$Cr(O_2CH)_2(H_2O)_{2.5}$", was said to have the same crystal form as its precursor. In the course of this work, we confirmed that drying of $Cr(O_2CH)_2(H_2O)_{8/3}$ does yield a product that appears to the eye to consist of cubic crystals. Closer examination, however, showed that these were in fact opaque, and they gave no diffraction pattern in rotation photographs. While the compound produced in this manner may well have the simple formula $Cr_2(O_2CH)_4(H_2O)_2$, it is not evident that there is any way to obtain crystals of it. In any event, we anticipate no further work on the material, since the information available from it should be no different from that obtained in the present case; the molecular structure is probably very similar to that of the Cr(1) dimer shown in Figure 1.

The disparity in the Cr–L_{ax} distance in the independent $Cr_2(O_2CH)_4$ moieties is puzzling. Work in this laboratory has shown that for molecules of the type $Cr_2(O_2CR)_4(L_{ax})_2$, with a given R, *d*(Cr–Cr) generally increases as *d*(Cr–L_{ax}) decreases.[4] The bond lengths *d*[Cr(1)–Cr(1′)] and *d*[Cr(1)–O(15)] produce a point which falls quite nicely into the anticipated range, but the very short Cr(2)–O(23) distance of 2.210 (6) Å would be expected to produce a much longer Cr(2)–Cr(2′) bond. The only apparent chemical difference in the dimers is that O(15) appears to be involved in three hydrogen bonds while O(23) has no more than two.

Thus, the structural data presented here only add to the rather confusing picture with respect to how Cr–Cr distances in these carboxylates are influenced by various other characteristics of the molecule, such as the electronic nature of R and the strength of binding of axial ligands.

Finally, the difficulty encountered in refining the structure to a reasonable set of interatomic distances deserves brief comment. Although the problem of false minima, or false solutions, is sometimes considered in the early stages of the solution of a structure, there appear to be few if any other instances of two complete, stable solutions based on the same data which give such markedly different residuals with such small alterations in the parameters. The ratio of observations to variables, 1168/133 = 8.8, would ordinarily be considered to afford an adequate degree of overdetermination. We are unable to suggest a reason for the observed behavior. We shall, however, offer the suggestion that even the most efficient methods of computation are best used as adjuncts to a sense of the chemically reasonable rather than as a substitute for it.

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Registry No. $[Cr_2(O_2CH)_4(H_2O)_2]_3(H_2O)_{10}$, 65366-48-5.

Supplementary Material Available: Tables of structure factors and a table of atom parameters for the false minimum (11 pages). Ordering information is given on any current masthead page.

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(6) Computer programs used on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Tex., were those of the Enraf-Nonius structure determination package.
(7) We are especially grateful to Dr. Jan Troup for helpful discussions on this matter.
(8) Supplementary material.

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Reactions and Reaction Products of Bromine and Iodine with Tetrakis(ethyl xanthato)dimolybdenum(*4° Mo-Mo*)

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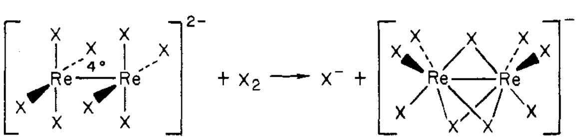
The reactions of Br_2 and I_2 with $Mo_2(S_2COC_2H_5)_4$ produce crystalline solids with the composition $Mo_2(S_2COC_2H_5)_4X_2$, both of which have been fully characterized by x-ray crystallography. They are isomorphous, crystallizing in space group $P2_1/c$ with the following unit cell dimensions, where the two figures refer first to the bromide and second to the iodide: a = 12.355 (3), 12.538 (2) Å; b = 8.885 (2), 8.897 (1) Å; c = 12.835 (3), 13.279 (3) Å; β = 115.18 (1), 115.71 (1)°; V = 1275.1 (8), 1334.6 (4) Å^3; Z = 2. The structures were solved and refined to residuals (R_1, R_2) of 0.038, 0.050 for the bromide and 0.025, 0.038 for the iodide. Each half of the centrosymmetric dinuclear molecule consists of a nearly planar $Mo(S_2COEt)_2$ unit with a halogen atom bonded perpendicular to the mean MoS_4 plane. These halves are then joined with each molybdenum atom lying over one of the S_2C groups of the other half so that it is bonded to both S atoms (mean Mo-S, 2.44 Å) and the C atom (2.302 Å). The S_2C group plane is approximately prependicular to the extension of the X-Mo line so that the coordination of Mo can be described as roughly octahedral, provided the "side-on" S_2C group is considered to occupy one coordination site. In addition, there is a metal-metal bond (Mo-Mo, 2.720 (3) Å) which can be thought of as a single bond that completes an 18-electron configuration about each Mo atom. The Mo-Br and Mo-I bonds are unusually long (2.627 (2) and 2.852 (1) Å, respectively). The bridging S_2COR groups, forming a total of five bonds, are unprecedented for either xanthato or dithiocarbamato ligands. The reactivity of the $Mo_2(S_2COC_2H_5)_4X_2$ compounds with a variety of reagents has been examined.

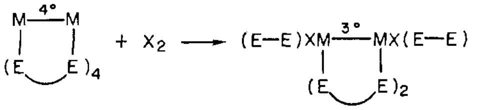
Introduction

The first attempts to oxidize species containing metal-to-metal quadruple (4°M-M) bonds with halogens, namely, by the action of X_2 (X = Cl, Br) on the $Re_2X_8^{2-}$ ions, were reported some 10 years ago.[1] These reactions resulted in extensive structural rearrangement accompanied by considerable reduction in the M-M bond strength as indicated in eq 1. The $Re_2Cl_9^-$ anion has been shown[2] to have an Re-Re distance of 2.70 Å, indicative of only a weak bond between the rhenium atoms. The reaction can be thought of formally as a combination of an oxidative addition and a rearrangement that includes expulsion of one X^- ligand.



(1)

We have recently taken a renewed interest in oxidative addition reactions as possible ways of preparing triple M-M bonds from quadruple M-M bonds. This is particularly pertinent in view of the discovery that certain compounds, e.g., $W_2(O_2CNR_2)_2(\mu\text{-}O_2CNR_2)_2X_2$, with triple W-W bonds have five-coordinated metal atoms. This suggests the possibility that reactions of the type (2) might provide a method, conceivably a fairly general one, for conversion of quadruple M-M to triple M-M. We are presently testing this idea with a variety of compounds.



$$M\overset{4°}{\text{—}}M(E\text{—}E)_4 + X_2 \longrightarrow (E\text{—}E)XM\overset{3°}{\text{—}}MX(E\text{—}E)\ (E\text{—}E)_2$$

(2)

In the case where the bidentate, uninegative ligand, EE, is ethyl xanthate, $EtOCS_2^-$, and M = Mo, the reaction does not follow the simple course shown in eq 2 in the structural sense although the stoichiometry is as shown. We describe in detail here the chemical and x-ray crystallographic investigation of the reactions in which X_2 represents Br_2 and I_2. The starting material, $Mo_2(S_2COC_2H_5)_4$, is already a well-characterized compound.[3]

Experimental Section

Materials and Methods. $Mo_2(O_2CCH_3)_4$ was prepared according to an established procedure.[4] $KS_2COC_2H_5$ and $KS_2COCH(CH_3)_2$ were prepared by adding CS_2 to an alcoholic solution of KOH. All other compounds and solvents were of reagent grade or better, from commercial sources.

Carbon and hydrogen analyses were performed at the Center for Trace Characterization, Texas A&M University.

All reactions involving molybdenum compounds were performed under nitrogen using air-tight glassware. All solvents were dried over molecular sieves and deoxygenated prior to use.

Preparation of $Mo_2(xan)_4$. The reported procedure[3] calls for the addition of a large excess of potassium ethyl xanthate to dimolybdenum tetraacetate in ethanol. Using this method, a considerable amount of a green impurity was always present. However, if only an equivalent amount of the xanthate is used, the reaction produces no noticeable amount of this impurity. In a typical reaction, $Mo_2(O_2CCH_3)_4$ (3.30 g, 7.5 mmol) was added to 350 mL of absolute ethanol. To this was added $KS_2COC_2H_5$ (4.8 g, 30 mmol). The mixture was stirred for 6–12 h at room temperature. The product was then filtered, washed

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