weak intermolecular axial interactions (Mo···O, 2.72 Å) by considerably shorter bonds to a stronger base (Mo···N, 2.55 Å) is accompanied by an increase of 0.039 (4) Å in the Mo–Mo distance. It seems reasonable to presume a cause and effect relationship.

However, the effect seen in the case of the trifluoroacetate may well be atypically large in view of the result we now have in comparing the benzoate and its diglyme adduct. In the former the axial intermolecular contacts are rather weak (Mo···O, 2.88 Å) while in the latter a diglyme oxygen atom is coordinated in each molybdenum atom considerably more closely (2.66 Å) although still not so strongly as is the pyridine nitrogen atom in $Mo_2(O_2CCF_3)_4{\cdot}2C_5H_5N$. There is an apparent slight increase in the Mo–Mo quadruple bond distance, 0.004 (1.5) Å, but it is on the threshold of statistical or chemical significance.

Thus, we conclude that axial coordination can affect the strength of the Mo–Mo quadruple bond but that only in special cases, i.e., where R is very electron withdrawing and L is a very good donor (factors that should operate synergistically) will the lengthening of the Mo–Mo quadrupole bond be more than marginal.

As we shall show in a forthcoming paper[10] this rigidity or toughness of the Mo–Mo quadruple bond is in dramatic contrast to the ease with which the length of the Cr–Cr quadruple bond in analogous compounds can be altered.

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Supplementary Material Available: Tables of observed and calculated structure factors for both $Mo_2[O_2CC(CH_3)_3]_4$ and $Mo_2(O_2CPh)_4$ (20 pages). Ordering information is given on any current masthead page.

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Sensitivity of the Chromium–Chromium Quadruple Bond in Dichromium Tetracarboxylates to Axial Coordination and Changes in Inductive Effects

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X-ray crystallographic studies have been made of six $Cr_2(O_2CR)_4L_2$-type compounds to determine the response of the Cr–Cr quadruple bond, as that response is evidenced in the bond length, to (a) the closeness of axial ligand atoms and (b) the inductive character of the R groups. The new results together with others already in the literature (for a total of 8 compounds) show that the Cr–Cr quadruple bond is very sensitive to both of these factors and evidently to others as well, since no simple, qualitative trends are apparent. The new structures reported here are those of the following compounds, where the numbers in parentheses following each formula are the lengths in Å of the Cr–Cr and the Cr–(axial ligand) bonds: (I) $Cr_3(O_2CH)_6(H_2O)_2$ (2.451, 2.224); (II) $Cr_2(O_2CH)_4(C_5H_5N)_2$ (2.408, 2.308); (III) $Cr_2(O_2CCF_3)_4(Et_2O)_2$ (2.541, 2.244); (IV) $Cr_2(O_2CCMe_3)_4$ (2.388, 2.44); (V) $Cr_2(O_2CPh)_4(PhCO_2H)_2$ (2.352, 2.295); (VI) Cr_2(9-anthracenecarboxylate)$_4$-$(CH_3OCH_2CH_2OCH_3)$ (2.283, 2.283). It is concluded that the Cr–Cr quadruple bond interaction, within the tetra-μ-carboxylato environment, must be described by a very broad, relatively shallow potential function so that the Cr–Cr distance is easily varied over a broad range by a variety of additional factors. It is shown that the variations in Cr–Cr distance cannot be accounted for solely by postulating linear and independent dependences on the inductive effect of the R groups and the distances to the axial ligand atoms.

Introduction

The chemistry of compounds containing multiple bonds between metal atoms has developed rapidly since the recognition, in the early 1960s, of the first double bond,[1] the first triple bond,[2] and the first quadruple bond.[3] With several of the elements that have a consistent tendency to form such bonds, particularly molybdenum and rhenium, the structural patterns are relatively simple, especially with respect to the quadruple bonds. In these cases, the Mo_2^{4+} and Re_2^{6+} central units appear to be structurally rigid, and the observed variation in metal–metal distance is relatively slight. Thus the Mo–Mo quadruple bond lengths span a range from 2.088 (1) in $Mo_2(O_2CCMe_3)_4$[4] to 2.183 (2) Å in $Mo_2(C_3H_5)_4$,[5] and the known range of Re–Re quadruple bond lengths is from 2.178 (1) in the $Re_2Me_8^{2-}$ ion[6] to about 2.24 Å in several compounds,[7] e.g., $Re_2Cl_8^{2-}$ salts.

With chromium, however, the situation is not so simple. Prior to the work described here, Cr–Cr quadruple bond distances have been reported as low as about 1.98 Å in the $Cr_2Me_8^{4-}$ and $Cr_2(CH_2CH_2CH_2CH_2)_4^{4-}$ ions[8,9] and $Cr_2(C_3$-

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Table I

(A) Positional and Thermal Parameters for $Cr_2(O_2CH)_6(H_2O)_2$ (I)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr(1)	1.00000 (0)	0.00000 (0)	0.00000 (0)	0.0065 (1)	0.00553 (10)	0.0124 (2)	−0.0050 (2)	−0.0022 (3)	0.0061 (2)
Cr(2)	0.51738 (7)	0.34548 (6)	0.40333 (8)	0.0077 (1)	0.00454 (7)	0.0086 (1)	−0.0050 (1)	−0.0025 (2)	0.0032 (1)
O(1)	0.8073 (4)	0.0009 (3)	−0.2328 (4)	0.0132 (5)	0.0111 (3)	0.0220 (6)	−0.0153 (6)	−0.0165 (10)	0.0179 (7)
O(2)	0.8680 (4)	−0.1243 (3)	0.1174 (4)	0.0101 (5)	0.0081 (3)	0.0171 (6)	−0.0064 (6)	0.0021 (9)	0.0092 (7)
O(3)	0.5433 (4)	0.0645 (3)	0.2517 (4)	0.0117 (5)	0.0052 (3)	0.0191 (7)	−0.0068 (6)	−0.0013 (10)	0.0026 (8)
O(4)	0.7846 (4)	0.3087 (3)	0.2507 (4)	0.0096 (5)	0.0059 (3)	0.0128 (5)	−0.0047 (6)	0.0021 (9)	0.0016 (7)
O(5)	0.7546 (4)	0.5896 (3)	0.4305 (4)	0.0117 (5)	0.0068 (3)	0.0145 (6)	−0.0084 (6)	0.0034 (10)	0.0008 (7)
O(6)	0.3557 (4)	0.4285 (3)	0.1890 (4)	0.0154 (6)	0.0085 (4)	0.0130 (5)	−0.0092 (7)	−0.0138 (10)	0.0071 (7)
O(7)	0.3246 (4)	0.7106 (3)	0.3633 (4)	0.0170 (6)	0.0077 (3)	0.0148 (5)	−0.0080 (7)	−0.0110 (10)	0.0121 (6)
C(1)	0.6892 (6)	−0.0840 (5)	0.1973 (6)	0.0129 (7)	0.0074 (5)	0.0146 (8)	−0.0102 (8)	−0.001 (1)	0.0062 (9)
C(2)	0.8497 (5)	0.4326 (5)	0.2992 (6)	0.0100 (7)	0.0085 (5)	0.0115 (8)	−0.0071 (9)	−0.000 (1)	0.0042 (10)
C(3)	0.2911 (6)	0.5883 (5)	0.2143 (6)	0.0179 (9)	0.0102 (5)	0.0118 (8)	−0.0092 (11)	−0.010 (1)	0.0105 (10)

(B) Bond Distances and Angles for $Cr_3(O_2CH)_6(H_2O)_2$ (I)[a]

Bond Distances, Å

Cr(2′)-Cr(2)	2.451 (1)	Cr(2′)-O(7)	2.026 (2)	O(2)-C(1)	1.250 (4)
Cr(2)-O(3)	2.224 (2)	Cr(1)-O(1)	2.063 (2)	O(3)-C(1)	1.249 (4)
Cr(2)-O(4)	2.027 (2)	Cr(1)-O(2)	2.022 (2)	O(4)-C(2)	1.257 (4)
Cr(2′)-O(5)	2.022 (2)	Cr(1)-O(4)	2.499 (2)	O(5)-C(2)	1.260 (4)
Cr(2)-O(6)	2.014 (2)			O(6)-C(3)	1.244 (4)
				O(7)-C(3)	1.268 (5)

Bond Angles, Deg

Cr(2′)-Cr(2)-O(3)	175.60 (7)	Cr(2)-O(3)-C(1)	134.6 (2)	O(4)-Cr(2)-O(6)	90.7 (1)
Cr(2′)-Cr(2)-O(4)	86.58 (7)	Cr(2)-O(4)-C(2)	120.6 (2)	O(4)-Cr(2)-O(7′)	89.2 (1)
Cr(2)-Cr(2′)-O(5)	87.30 (7)	Cr(2′)-O(5)-C(2)	120.0 (2)	O(5)-Cr(2′)-O(6′)	88.2 (1)
Cr(2′)-Cr(2)-O(6)	87.22 (7)	Cr(2)-O(6)-C(3)	120.4 (2)	O(5)-Cr(2′)-O(7)	91.2 (1)
Cr(2)-Cr(2′)-O(7)	86.70 (7)	Cr(2′)-O(7)-C(3)	119.7 (2)	Cr(1)-O(2)-C(1)	133.6 (2)
O(1)-Cr(1)-O(1)	180	O(3)-Cr(2)-O(4)	96.4 (1)	Cr(1)-O(4)-Cr(2)	117.5 (1)
O(2)-Cr(1)-O(2)	180	O(3)-Cr(2)-O(5′)	89.8 (1)	Cr(1)-O(4)-C(2)	121.4 (2)
O(4)-Cr(1)-O(4)	180	O(3)-Cr(2)-O(6)	96.0 (1)	Cr(2)-O(4)-C(2)	120.6 (2)
O(1)-Cr(1)-O(2)	92.0 (1)	O(3)-Cr(2)-O(7′)	90.1 (1)	O(2)-C(1)-O(3)	126.7 (3)
O(1)-Cr(1)-O(4)	94.9 (1)	O(4)-Cr(2)-O(5′)	173.8 (1)	O(4)-C(2)-O(5)	125.3 (3)
O(2)-Cr(1)-O(4)	95.8 (1)	O(6)-Cr(2)-O(7′)	173.9 (1)	O(6)-C(3)-O(7)	125.9 (3)

[a] The atom-numbering scheme is shown in Figure 1. Primed atoms are related to unprimed ones by inversion through $^1/_2$, $^1/_2$, $^1/_2$.

Table II

(A) Positional and Thermal Parameters for $Cr_2(O_2CH)_4(C_5H_5N)_2$ (II)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.10407 (6)	0.02464 (6)	0.08098 (8)	0.00467 (5)	0.00441 (5)	0.00916 (9)	−0.00019 (9)	−0.0005 (1)	−0.0003 (1)
O(1)	0.0183 (3)	−0.0070 (3)	0.2982 (4)	0.0064 (3)	0.0082 (3)	0.0097 (4)	−0.0021 (5)	−0.0002 (6)	−0.0005 (6)
O(2)	−0.1758 (3)	−0.0514 (3)	0.1484 (4)	0.0062 (3)	0.0078 (3)	0.0112 (5)	−0.0013 (5)	0.0015 (6)	0.0005 (6)
O(3)	0.0401 (3)	0.1961 (3)	0.0802 (4)	0.0073 (3)	0.0042 (2)	0.0175 (5)	0.0006 (5)	−0.0037 (7)	−0.0015 (7)
O(4)	−0.1533 (3)	0.1503 (3)	−0.0694 (4)	0.0071 (3)	0.0054 (3)	0.0163 (5)	0.0009 (5)	−0.0040 (7)	−0.0007 (7)
N	0.3029 (3)	0.0744 (3)	0.2361 (4)	0.0052 (3)	0.0059 (3)	0.0122 (5)	0.0001 (6)	−0.0007 (7)	−0.0005 (8)
C(1)	−0.1007 (5)	−0.0382 (4)	0.2890 (6)	0.0084 (4)	0.0063 (4)	0.0113 (7)	−0.0004 (7)	0.0027 (9)	−0.0000 (9)
C(2)	−0.0728 (4)	0.2215 (4)	0.0081 (6)	0.0074 (4)	0.0060 (4)	0.0164 (8)	0.0014 (7)	−0.0022 (10)	−0.0008 (10)
C(3)	0.4113 (5)	0.0150 (5)	0.2076 (6)	0.0072 (4)	0.0080 (4)	0.0152 (8)	0.0027 (7)	0.0003 (10)	−0.0002 (10)
C(4)	0.5364 (4)	0.0522 (6)	0.2760 (7)	0.0054 (4)	0.0122 (6)	0.0216 (10)	0.0019 (9)	0.0006 (11)	0.0005 (13)
C(5)	0.5478 (5)	0.1522 (6)	0.3786 (7)	0.0080 (5)	0.0121 (6)	0.0206 (10)	−0.0052 (9)	−0.0039 (12)	0.0003 (14)
C(6)	0.4361 (6)	0.2128 (5)	0.4122 (7)	0.0111 (5)	0.0094 (5)	0.0171 (9)	−0.0045 (9)	−0.0024 (11)	−0.0048 (11)
C(7)	0.3148 (5)	0.1712 (4)	0.3364 (6)	0.0089 (4)	0.0058 (4)	0.0133 (7)	−0.0007 (7)	0.0014 (10)	−0.0027 (9)

(B) Bond Distances and Angles for $Cr_2(O_2CH)_4(C_5H_5N)_2$ (II)[a]

Bond Distances, Å

Cr-Cr′	2.408 (1)	O(1)-C(1)	1.260 (5)	N-C(7)	1.330 (5)
Cr-N	2.308 (3)	O(2)-C(1)	1.267 (4)	C(3)-C(4)	1.391 (6)
Cr-O(1)	2.012 (3)	O(3)-C(2)	1.256 (4)	C(4)-C(5)	1.368 (7)
Cr-O(2)	2.018 (2)	O(4)-C(2)	1.248 (5)	C(5)-C(6)	1.377 (7)
Cr-O(3)	2.024 (3)	N-C(3)	1.332 (5)	C(6)-C(7)	1.390 (6)
Cr-O(4)	2.023 (3)				

Bond Angles, Deg

Cr′-Cr-N	179.29 (9)	Cr-N-C(3)	119.6 (2)	O(2′)-Cr-O(4′)	89.3 (1)
Cr′-Cr-O(1)	87.26 (7)	Cr-N-C(7)	121.2 (2)	O(1)-Cr-N	92.8 (1)
Cr-Cr′-O(2)	87.89 (7)	C(3)-N-C(7)	118.6 (3)	O(2′)-Cr-N	92.1 (1)
Cr′-Cr-O(3)	87.06 (7)	N-C(3)-C(4)	122.3 (4)	O(3)-Cr-N	92.2 (1)
Cr-Cr′-O(4)	88.01 (7)	N-C(7)-C(6)	122.5 (4)	O(4′)-Cr-N	92.7 (1)
Cr-O(1)-C(1)	120.7 (2)	O(1)-Cr-O(2′)	175.1 (1)	O(1)-C(1)-O(2)	124.6 (3)
Cr′-O(2)-C(1)	119.5 (2)	O(3)-Cr-O(4′)	175.1 (1)	O(3)-C(2)-O(4)	126.2 (4)
Cr-O(3)-C(2)	119.7 (2)	O(1)-Cr-O(3)	89.9 (1)	C(3)-C(4)-C(5)	118.7 (4)
Cr′-O(4)-C(2)	119.0 (2)	O(1)-Cr-O(4′)	90.1 (1)	C(4)-C(5)-C(6)	119.5 (4)
		O(2′)-Cr-O(3)	90.4 (1)	C(5)-C(6)-C(7)	118.4 (4)

[a] The atom-numbering scheme is shown in Figure 2. Primed atoms are related to unprimed ones by inversion.

$H_5)_4$[10,11] and as high as 2.362 Å in $Cr_2(O_2CCH_3)_4(H_2O)_2$,[12] with many intermediate ones; e.g., 2.22 in the $Cr_2(CO_3)_4^{4-}$ ion,[13] 2.288 in $Cr_2(O_2CCH_3)_4$,[14] 2.100 in $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$,[15] and 2.214 Å in $Cr_2(C_8H_8)_3$.[16]

It was even proposed[17] at one time that in $Cr_2(O_2CCH_3)_4(H_2O)_2$ and other carboxylato compounds there is *no* Cr–Cr bond, but this has been conclusively refuted.[18,19] The true situation is that the Cr–Cr quadruple bond interaction, in great contrast to the homologous Mo–Mo interaction, is very sensitive to its environment and is capable of varying greatly in strength and, therefore, in Cr–Cr distance. Within the class of compounds of general formula $Cr_2(O_2CR)_4L_2$, we have already seen[14] that the strength of the Cr–(axial ligand) bonds has an important effect (as compared to the very minor one in the Mo_2 systems[4]) on the Cr–Cr bond length by comparison of $Cr_2(O_2CCH_3)_4(H_2O)_2$, which has Cr–Cr and Cr··O(axial) distances of 2.362 and 2.272 Å, with $Cr_2(O_2CCH_3)_4$, where the corresponding distances are 2.288 and 2.327 Å.

The objective of the work reported here was to explore more extensively the dependence of Cr–Cr bond length on variations in the two parameters available within the general formula $Cr_2(O_2CR)_4L_2$, namely, the nature of R, especially its electron-donating or -withdrawing power, and the nature and proximity of the axial ligand, L. It is to be noted that, as with the molybdenum compounds, L may be absent, but in that case there is still some axial interaction provided by oxygen atoms of neighboring molecules. That situation will be seen here in the case of $Cr_2(O_2CCMe_3)_4$. To accomplish our objective we have determined the crystal structures of a number of chromium(II) carboxylate compounds. Six of them, which give at least a preliminary idea of how these systems behave, are reported and discussed here.

Procedures

Preparation. Reactions and manipulations involving oxidation-sensitive chromium(II) solutions and compounds were carried out under atmospheres of argon or nitrogen or, in the case of selecting and mounting crystals for X-ray studies, under a layer of heavy, degassed mineral oil. With the exceptions of I and II, these compounds are also moisture sensitive, and appropriate precautions were taken to exclude water from the reaction systems.

Benzoic acid, pivalic acid (Me_3CCO_2H), and anthracene-9-carboxylic acid were purchased from Aldrich and used without further purification.

Chromocene, Cp_2Cr ($Cp = C_5H_5$), was prepared by a modification of the method reported by King.[20] LiCp, prepared in situ from BuLi and CpH, was used instead of NaCp. The Cp_2Cr was purified by extracting it from the crude reaction mixture with warm hexane, removing the hexane, and then subliming the Cp_2Cr in vacuo (50–80 °C, 10^{-3} cm Hg).

$Cr_3(O_2CH)_6(H_2O)_2$ (I). The synthesis was adapted from that reported by Herzog and Kalies[21] for "$Cr(O_2CH)_2(H_2O)$". A solution of 10.0 g (38 mmol) of $CrCl_3 \cdot 6H_2O$ in 30 mL of dilute HCl was added, through a Jones reductor column, to 5.4 g (86 mmol) of NH_4O_2CH. The first addition of chromium(II) to the ammonium formate gave a transient red color which was replaced, first, by a purple solution and then by a purple gel. The gel was diluted with 10 mL of water and heated for 20 min in a boiling water bath to obtain a homogenous solution. Slow cooling yielded the product as large, well-formed red needles and blocks.

$Cr_2(O_2CH)_4(C_5H_5N)_2$ (II). Compound I, prepared as just described from 89 mmol of NH_4O_2CH and 38 mmol of $CrCl_3 \cdot 6H_2O$, was washed twice with a small amount of water, dissolved in 40 mL of water, and filtered into a clean flask. The solution was covered with 50 mL of hexane. A solution of 3.0 mL (37 mmol) of pyridine in 40 mL of hexane was carefully added to the hexane layer. The flask was allowed to stand undisturbed so as to permit slow diffusion of pyridine into the chromium(II) formate solution. After 3 days, the aqueous layer contained large single crystals (dimensions up to 1.5 mm) of the dark red product.

$Cr_2(O_2CCF_3)_4[O(C_2H_5)_2]_2$ (III). To a suspension of 1.3 g (2.8 mmol) of $(NH_4)_4(Cr_2(CO_3)_4(H_2O)_3)$[22] in 50 mL of diethyl ether was added 1.2 mL (15 mmol) of CF_3CO_2H. The mixture was refluxed for 1 h, to convert the slurry of the yellow carbonate complex to a purple solution. The solvent was then stripped from the solution, and the residue was dried for 12 h under vacuum to ensure the removal of excess trifluoroacetic acid. This solid was extracted with 15 mL of boiling benzene which was filtered while warm into a clean Schlenk tube. The tube was closed with a stopper and suspended in a Dewar vessel above ice, so heat transfer occurred primarily by conduction through air. After 3 days, the tube contained large single crystals with dimensions up to 2 mm. The crystals were of good optical quality despite a lack of well-defined faces. When viewed through a single polarizer, the crystals were very deep purple in random orientations, but at a particular angle to the polarizer they were transparent and virtually colorless.

$Cr_2(O_2CCMe_3)_4$ (IV). Cp_2Cr (343 mg, 1.88 mmol) and Me_3CCO_2H (383 mg, 3.75 mmol) were placed in a round bottom flask and dissolved in dry, degassed benzene.[23] An immediate reaction occurred. Upon standing overnight, a mass of very fine red crystals formed, leaving a nearly colorless solution. The product was filtered and dried in vacuo. Crystals were grown by sublimation in a sealed tube (ca. 190 °C (10^{-2} Torr)).

$Cr_2(O_2CPh)_4(PhCO_2H)_2$ (V). Cp_2Cr (0.5 g, 2.8 mmol) and $PhCO_2H$ (1.0 g, 8.2 mmol) were dissolved in toluene. An immediate reaction occurred and red crystals came out of solution. The crystals were filtered off and dried in vacuo.

Cr_2(anthracene-9-carboxylate)$_4$DME (VI). Cp_2Cr (154 mg, 0.88 mmol) and anthracene-9-carboxylic acid (377 mg, 1.69 mmol) were dissolved in 30 mL of DME (1,2-dimethoxyethane) and allowed to stand, undisturbed, at room temperature for 30 days. The red crystals which had slowly formed were filtered off and dried in vacuo.

X-Ray Data Collection. Since chromium(II) compounds are sensitive to air oxidation, crystals were generally mounted in glass capillaries either by wedging them into mineral oil-filled capillaries of the proper size or by placing them in an epoxy-cement matrix in slightly over-sized capillaries.

Data were collected on a Syntex $P\bar{1}$ automated four-circle diffractometer using Mo Kα ($\lambda = 0.710730$ Å) radiation with a graphite-crystal monochromator, mounted in the equatorial mode, in the incident beam. The details of the automatic centering and indexing procedures used to produce orientation matrices for data collection have been described previously.[24] In general, 15 strong, low-angle reflections ($4° < 2\theta < \sim 20°$) were used to determine an initial orientation matrix for a crystal. Subsequently, 15 higher angle reflections, generally in the range $20° < 2\theta < 30°$, were used to obtain cell constants of satisfactory precision.

Most of the data were collected by the following standard method. The diffractometer was operated at 22 ± 2° using the θ–2θ scan technique with a variable scan rate from 4.0 to 24.0°/min. The scan range was from 2θ(Mo Kα_1) − 1.0° to 2θ(Mo Kα_2) + 1.0°. Stationary crystal/counter background counts were taken at each end of the 2θ scan range, with a background to scan time ratio of 0.5. The intensities of three or more standard reflections were measured periodically as a check on the stability of the crystals and counting equipment. Variations of this standard procedure, required for particular crystals, were as follows: The crystal of III, though the best of a fairly poor lot, had peaks whose ω scan gave full widths at half-maximum of ca. 0.4°, requiring a 2θ scan range from 2θ(Mo Kα_1) − 1.5° to 2θ(Mo Kα_2) + 1.5°.

Over a dozen crystals of IV, which gave extremely broad and usually split ω scans, even though they appeared to be well formed, were examined before a rather small but acceptable crystal was found. The ω scans of 15 intense, low-angle reflections varied in width from 0.2 to 0.4° and showed no splittings greater than 0.1°. No changes were made in the above-mentioned standard data collection procedure. The crystal of V diffracted poorly; ω scans had peak widths at half-height of ca. 0.4°. Scan speeds of from 4 to 24°/min were used for $0° < 2\theta < 32°$ and from 2 to 24°/min for $32° < 2\theta < 45°$ with $\theta/2\theta$ scans ranging from 2θ(Mo Kα_1) − 1.3° to 2θ(Mo Kα_2) + 1.3°.

Crystallographic data for all six compounds, as well as details of data collection and refinement, e.g., the numbers of measured reflections, crystal sizes, 2θ ranges, and R values, are given in Table VII. In each case Lorentz and polarization corrections were applied to the intensity data,[25] but no absorption corrections were deemed necessary in view of the low linear absorption coefficients. No corrections for crystal decay were required.

Solution and Refinement of the Structures.[25] The procedure employed for the solution of the structure of $Cr_3(O_2CH)_6(H_2O)_2$, I,

Table III

(A) Positional and Thermal Parameters for $Cr_2(O_2CCF_3)_4(Et_2O)_2$ (III)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.09075 (6)	0.06694 (6)	0.00637 (7)	0.01610 (7)	0.01217 (6)	0.01386 (8)	−0.0120 (1)	0.0068 (1)	−0.0015 (1)
F(1)	−0.1746 (4)	0.1214 (3)	0.4864 (3)	0.0446 (6)	0.0251 (5)	0.0214 (4)	−0.0179 (8)	0.0379 (7)	−0.0051 (7)
F(2)	−0.0482 (5)	0.2474 (4)	0.4779 (4)	0.0535 (7)	0.0478 (6)	0.0273 (5)	−0.0572 (10)	0.0359 (10)	−0.0440 (9)
F(3)	−0.2790 (5)	0.3153 (4)	0.3390 (4)	0.0487 (8)	0.0239 (5)	0.0279 (6)	0.0271 (12)	0.0285 (11)	0.0021 (9)
F(4)	0.3367 (4)	−0.4435 (3)	0.3295 (4)	0.0307 (5)	0.0196 (4)	0.0343 (6)	−0.0082 (7)	0.0088 (10)	0.0216 (8)
F(5)	0.4810 (4)	−0.3264 (4)	0.3575 (4)	0.0274 (5)	0.0244 (5)	0.0322 (6)	−0.0105 (8)	−0.0180 (10)	0.0063 (10)
F(6)	0.4501 (4)	−0.4358 (4)	0.1456 (4)	0.0355 (6)	0.0255 (6)	0.0278 (5)	0.0161 (11)	0.0236 (9)	−0.0057 (9)
O(1)	0.0135 (3)	0.1515 (3)	0.2028 (3)	0.0221 (4)	0.0156 (3)	0.0155 (4)	−0.0162 (5)	0.0100 (7)	−0.0065 (6)
O(2)	−0.1462 (3)	0.0349 (3)	0.1919 (3)	0.0195 (3)	0.0160 (3)	0.0165 (4)	−0.0143 (5)	0.0133 (6)	−0.0035 (6)
O(3)	0.2628 (3)	−0.1136 (3)	0.1380 (3)	0.0176 (4)	0.0142 (3)	0.0179 (4)	−0.0118 (5)	0.0041 (7)	0.0002 (6)
O(4)	0.1030 (3)	−0.2309 (3)	0.1286 (3)	0.0184 (4)	0.0130 (3)	0.0172 (4)	−0.0115 (5)	0.0059 (7)	0.0015 (6)
O(5)	0.2448 (4)	0.1902 (3)	0.0077 (5)	0.0275 (4)	0.0233 (4)	0.0349 (8)	−0.0334 (6)	0.0099 (10)	−0.0059 (9)
C(1)	−0.0871 (5)	0.1205 (4)	0.2495 (4)	0.0191 (6)	0.0130 (4)	0.0128 (5)	−0.0069 (8)	0.0073 (9)	0.0016 (8)
C(2)	−0.1491 (6)	0.2040 (5)	0.3903 (5)	0.0287 (8)	0.0161 (6)	0.0159 (6)	−0.0096 (11)	0.0137 (12)	−0.0042 (10)
C(3)	0.2341 (4)	−0.2199 (4)	0.1664 (4)	0.0170 (5)	0.0129 (4)	0.0126 (5)	−0.0064 (8)	0.0063 (9)	−0.0020 (8)
C(4)	0.3779 (5)	−0.3583 (5)	0.2522 (5)	0.0213 (7)	0.0136 (5)	0.0175 (6)	−0.0060 (9)	0.0032 (11)	0.0022 (10)
C(5)	0.3564 (11)	0.2106 (10)	0.1263 (13)	0.0901 (16)	0.0690 (13)	0.0534 (24)	−0.1280 (17)	−0.0293 (34)	0.0135 (31)
C(6)	0.3912 (10)	0.1515 (9)	0.2730 (11)	0.0665 (17)	0.0516 (13)	0.0453 (20)	−0.0804 (19)	−0.0236 (32)	0.0041 (28)
C(7)	0.2446 (8)	0.2504 (7)	−0.1471 (10)	0.0475 (10)	0.0313 (8)	0.0573 (18)	−0.0466 (11)	0.0414 (19)	0.0076 (19)
C(8)	0.1448 (10)	0.4076 (9)	−0.1661 (13)	0.0499 (16)	0.0345 (11)	0.0772 (28)	−0.0406 (18)	0.0163 (34)	0.0339 (27)

(B) Bond Distances and Angles for $Cr_2(O_2CCF_3)_4[O(C_2H_5)_2]_2$ (III)[a]

Bond Distances, Å

Cr–Cr′	2.541 (1)	O(2)–C(1)	1.234 (4)	C(5)–C(6)	1.32 (1)
Cr–O(1)	2.017 (2)	O(3)–C(3)	1.235 (4)	C(7)–C(8)	1.45 (1)
Cr′–O(2)	2.022 (2)	O(4)–C(3)	1.252 (4)	C(2)–F(1)	1.302 (5)
Cr–O(3)	2.013 (2)	O(5)–C(5)	1.367 (4)	C(2)–F(2)	1.286 (5)
Cr′–O(4)	2.017 (2)	O(5)–C(7)	1.470 (7)	C(2)–F(3)	1.265 (5)
Cr–O(5)	2.244 (3)	C(1)–C(2)	1.538 (5)	C(4)–F(4)	1.311 (5)
O(1)–C(1)	1.251 (4)	C(3)–C(4)	1.538 (5)	C(4)–F(5)	1.306 (5)
				C(4)–F(6)	1.310 (5)

Bond Angles, Deg

Cr′–Cr–O(1)	85.28 (7)	O(5)–C(5)–C(6)	120.8 (8)	O(1)–Cr–O(5)	95.8 (1)
Cr–Cr′–O(2)	85.79 (7)	O(5)–C(7)–C(8)	109.1 (7)	O(2′)–Cr–O(5)	93.1 (1)
Cr′–Cr–O(3)	85.78 (7)	C(1)–C(2)–F(1)	111.8 (3)	O(3)–Cr–O(5)	96.3 (1)
Cr–Cr′–O(4)	85.49 (7)	C(1)–C(2)–F(2)	112.3 (4)	O(4′)–Cr–O(5)	92.4 (1)
Cr′–Cr–O(5)	177.6 (1)	C(1)–C(2)–F(3)	110.4 (3)	O(1)–C(1)–C(2)	116.0 (3)
Cr–O(1)–C(1)	121.0 (2)	C(3)–C(4)–F(4)	112.9 (3)	O(2)–C(1)–C(2)	116.7 (3)
Cr′–O(2)–C(1)	120.5 (2)	C(3)–C(4)–F(5)	112.5 (3)	O(3)–C(3)–C(4)	116.2 (3)
Cr–O(3)–C(3)	120.5 (2)	C(3)–C(4)–F(6)	108.9 (3)	O(4)–C(3)–C(4)	115.8 (3)
Cr′–O(4)–C(3)	120.2 (2)	O(1)–Cr–O(2′)	171.1 (1)	F(1)–C(2)–F(2)	105.5 (4)
Cr–O(5)–C(5)	132.3 (5)	O(3)–Cr–O(4′)	171.3 (1)	F(1)–C(2)–F(3)	108.0 (4)
Cr–O(5)–C(7)	117.7 (3)	O(1)–Cr–O(3)	91.1 (1)	F(2)–C(2)–F(3)	108.6 (4)
O(1)–C(1)–O(2)	127.3 (3)	O(1)–Cr–O(4′)	88.6 (1)	F(4)–C(4)–F(5)	106.3 (3)
O(3)–C(3)–O(4)	127.9 (3)	O(2′)–Cr–O(3)	88.1 (1)	F(4)–C(4)–F(6)	107.4 (4)
C(5)–O(5)–C(7)	109.7 (6)	O(2′)–Cr–O(4′)	90.8 (1)	F(5)–C(4)–F(6)	108.6 (4)

[a] The atom-numbering scheme is shown in Figure 3. Primed atoms are related to unprimed ones by inversion.

is representative of the general method. For this triclinic structure, the space group chosen was $P\bar{1}$. A three-dimensional Patterson function yielded the positions of the two independent chromium atoms. With Cr(1) fixed upon the origin, two cycles of least-squares refinement served to adjust the scale factor and the position of Cr(2). The positions of the five oxygen atoms bound to Cr(2) were then calculated from the original Patterson map. Two cycles of least-squares refinement upon these coordinates gave discrepancy indices

$$R_1 = \Sigma \| F_o | - | F_c \| / | F_o | = 0.299$$

$$R_2 = [\Sigma w (\| F_o | - | F_c \|)^2 / \Sigma w | F_o |^2]^{1/2} = 0.415$$

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.[25]

A difference Fourier map revealed the positions of the remaining nonhydrogen atoms. The positions of all nonhydrogen atoms were refined in three full-matrix least-squares cycles using isotropic temperature factors and then in three further cycles using anisotropic temperature factors to obtain the final discrepancy indices reported.

For all structures reported here least-squares refinement of the final model was continued until convergence had occurred. Refinement was deemed to have converged when, in the final cycle, no parameter shifted by more than 0.60 times its estimated standard deviation. When a refinement had converged, a final difference Fourier map was run to ensure that all atoms present had been included in the model. The heights of the largest peaks in these maps are mentioned in Table VII. Bond length and angle calculation indicated that the larger peaks were due to hydrogen atoms (I, II, and V) or to disorder of groups such as CF_3 and $O(C_2H_5)_2$ (III), CMe_3 (IV), or 1,2-dimethoxyethane (VI). In some cases, as can be seen from the tables of positional and thermal parameters, (Tables IA–VIA), not all of the atoms in a model were refined with anisotropic temperature factors.

The choice of space group was unequivocal for the triclinic species I, III, and IV, all of which were solved in the space group $P\bar{1}$, as well as for two of the monoclinic cases, II ($P2_1/c$) and V ($P2_1/n$). The correct choice of space group for VI ($P2_1/n$) was more difficult and is discussed below. Nonroutine aspects of the structure solutions are discussed below.

As refinement of the structure of IV was carried out it became obvious that one of the *tert*-butyl groups was disordered, but no simple model was found for this. C(44) and C(45) were refined at 0.5 occupancy since otherwise their thermal parameters became unrealistically large. However, we were unable to locate and refine the other "halves" of these methyl groups, although possible atoms were seen in difference Fourier maps. The largest peaks in the final difference map were in the area of the methyl groups and presumed to be due to some rotational disorder of the CMe_3 groups.

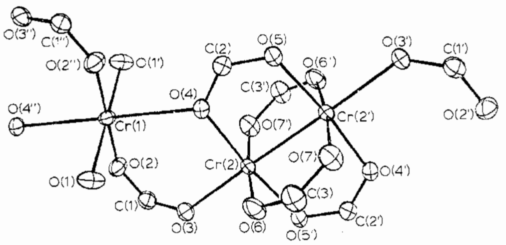

Figure 1. A representative portion of the structure of $Cr_3(O_2CH)_6(H_2O)_2$ (I) showing the single Cr atom at the origin, Cr(1), and the pair of Cr atoms, Cr(2) and Cr(2)′, making up the $Cr_2(O_2CH)_4$ motif. Atoms are represented by their thermal vibration ellipsoids drawn to enclose 50% of the electron density. The numbering scheme is shown and employs primed and unprimed numbers to designate pairs of atoms related by the center of inversion in the center of the $Cr_2(O_2CH)_4$ moiety and doubly primed and unprimed numbers for pairs of atoms related by the center of inversion at the origin.

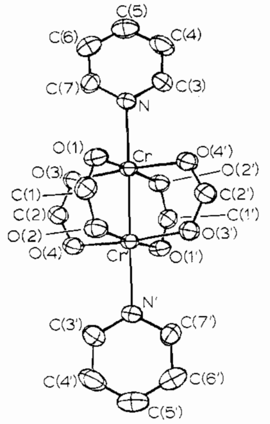

Figure 2. An ORTEP view of $Cr_2(O_2CH)_4(C_5H_5N)_2$ (II) using 50% probability ellipsoids. The numbering scheme is shown; the molecule has an inversion center and this relates atoms with primed numbers to those with the same unprimed numbers.

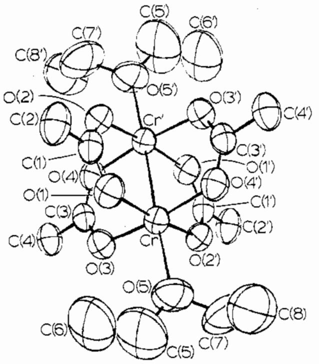

Figure 3. The $Cr_2(O_2CCF_3)_4(Et_2O)_2$ (III) molecule, with the F atoms omitted for clarity. The atom numbering scheme, which employs primed and unprimed numbers for pairs of atoms related by the center of inversion at the midpoint of the Cr–Cr bond, is defined.

The structure of VI was solved using the space group $P2_1$, there being several apparent violations to the expected additional systematic absences for the space group $P2_1/n$ ($h0l$; $h + l = 2n + 1$). When least-squares refinement failed to converge the structure utilizing the $P2_1$ space group, we examined the positional parameters and noted that the molecule appeared to possess a center of symmetry, which, at this point, was noncrystallographic. The structure was then successfully refined to convergence in $P2_1/n$ with the molecule lying on an inversion center. In either space group the solvent molecule is disordered rotationally. C(31) and C(32) represent an "average" of the CH_2 and CH_3 carbon atoms; thus the C–C bond is distorted. It was not possible to locate the individual disordered atoms. The only significant peak in the final difference Fourier map was in the region of the disordered solvent molecule.

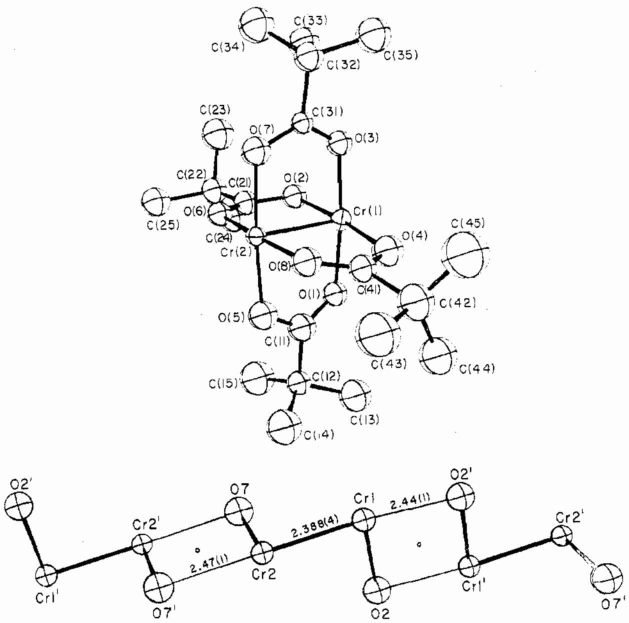

Figure 4. (a, top) An ORTEP view of the $Cr_2(O_2CCMe_3)_4$ (IV) molecule using 50% probability ellipsoids and showing the atom numbering scheme. The entire molecule is the asymmetric unit. (b, bottom) A projection of part of the structure of $Cr_2(O_2CCMe_3)_4$ (IV) perpendicular to the crystallographic *ac* plane, showing the mode of intermolecular axial interaction. Primed and unprimed atoms, labeled as in Figure 4a, are related by crystallographic inversion centers which lie between adjacent molecules.

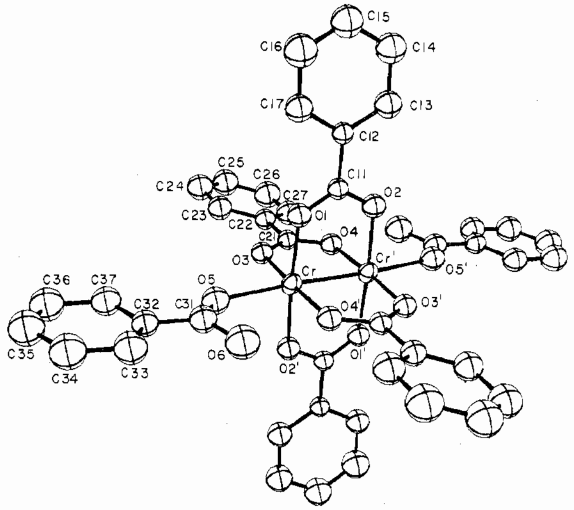

Figure 5. An ORTEP view of the $Cr_2(O_2CPh)_4(PhCO_2H)_2$ (V) molecule using 50% probability ellipsoids and showing the atom numbering scheme. The molecule possesses a crystallographic center of inversion that relates primed and unprimed atoms with the same number.

The final calculated and the observed structure factors for all six structures are available as supplementary material.

Results

The tables and figures giving the results are numbered according to the compounds they describe. Thus, Tables IA–VIA give the positional and thermal parameters for compounds I–VI, and Tables IB–VIB give bond lengths and angles. Each figure number (1–6) is the Arabic equivalent of the Roman numeral assigned to the compound. When two figures pertain to the same compound, each carries the appropriate number plus an a or b. The characteristics of individual compounds will now be described.

$Cr_3(O_2CH)_6(H_2O)_2$ (I). This substance[26] provides the first documented example of a compound containing both Cr_2^{4+}

Table IV

(A) Positional and Thermal Parameters for $Cr_2(O_2CCMe_3)_4$ (**IV**)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr(1)	0.5228 (3)	0.0783 (3)	0.8710 (3)	0.0061 (3)	0.0043 (3)	0.0048 (3)	−0.0053 (4)	0.0024 (5)	0.0002 (5)
Cr(2)	0.4556 (3)	0.0928 (3)	0.6248 (3)	0.0054 (3)	0.0034 (3)	0.0034 (3)	−0.0008 (4)	0.0020 (5)	−0.0005 (5)

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
O(1)	0.376 (1)	0.225 (1)	0.870 (1)	3.0 (3)	C(22)	0.250 (2)	−0.099 (2)	0.767 (2)	4.1 (6)
O(2)	0.414 (1)	−0.023 (1)	0.881 (1)	3.2 (3)	C(23)	0.332 (3)	−0.235 (2)	0.814 (3)	6.4 (8)
O(3)	0.662 (1)	−0.064 (1)	0.849 (1)	2.8 (3)	C(24)	0.168 (2)	−0.047 (2)	0.862 (3)	4.7 (6)
O(4)	0.619 (1)	0.186 (1)	0.845 (2)	4.1 (4)	C(25)	0.166 (2)	−0.096 (2)	0.611 (3)	5.0 (6)
O(5)	0.323 (1)	0.248 (1)	0.642 (2)	3.9 (4)	C(31)	0.676 (2)	−0.102 (2)	0.737 (2)	2.0 (4)
O(6)	0.347 (1)	0.001 (1)	0.652 (1)	3.1 (3)	C(32)	0.794 (2)	−0.210 (2)	0.740 (2)	3.5 (5)
O(7)	0.598 (1)	−0.060 (1)	0.623 (2)	3.6 (4)	C(33)	0.866 (2)	−0.188 (2)	0.641 (2)	3.3 (5)
O(8)	0.569 (1)	0.187 (1)	0.618 (1)	3.4 (3)	C(34)	0.739 (2)	−0.319 (2)	0.700 (3)	5.3 (7)
C(11)	0.312 (2)	0.284 (2)	0.759 (2)	3.9 (6)	C(35)	0.882 (2)	−0.235 (2)	0.897 (3)	5.0 (7)
C(12)	0.205 (2)	0.400 (2)	0.749 (2)	3.0 (5)	C(41)	0.618 (2)	0.221 (2)	0.725 (2)	3.1 (5)
C(13)	0.231 (2)	0.454 (2)	0.894 (3)	5.5 (7)	C(42)	0.693 (2)	0.313 (2)	0.735 (3)	4.9 (7)
C(14)	0.202 (2)	0.486 (2)	0.633 (3)	5.5 (7)	C(43)	0.672 (3)	0.360 (2)	0.588 (3)	6.2 (8)
C(15)	0.081 (3)	0.366 (3)	0.729 (3)	6.7 (8)	C(44)	0.622 (5)	0.414 (5)	0.798 (6)	5.3 (14)
C(21)	0.342 (2)	−0.031 (2)	0.766 (2)	3.3 (5)	C(45)	0.819 (6)	0.253 (5)	0.807 (7)	7.3 (18)

(B) Bond Distances and Angles in $Cr_2(O_2CCMe_3)_4$ (**IV**)[a]

Bond Distances, Å

Cr(1)-Cr(2)	2.388 (4)	C(11)-O(1)	1.25 (2)	C(41)-O(4)	1.28 (2)	C(22)-C(23)	1.60 (3)
-O(1)	2.01 (1)	-O(5)	1.27 (2)	-O(8)	1.21 (2)	-C(24)	1.52 (3)
-O(2)	2.04 (1)	-C(12)	1.52 (2)	-C(42)	1.59 (3)	-C(25)	1.61 (3)
-O(3)	1.99 (1)	C(21)-O(2)	1.26 (2)	O(1)-O(5)	2.21 (2)	C(32)-C(33)	1.54 (2)
-O(4)	2.03 (1)	-O(6)	1.24 (2)	O(2)-O(6)	2.23 (2)	-C(34)	1.64 (3)
-O(2)′	2.44 (1)	-C(22)	1.55 (3)	O(3)-O(7)	2.20 (2)	-C(35)	1.61 (3)
Cr(2)-O(5)	2.04 (1)	C(31)-O(3)	1.24 (2)	O(4)-O(8)	2.21 (2)	C(42)-C(43)	1.52 (3)
-O(6)	2.00 (1)	-O(7)	1.25 (2)	C(12)-C(13)	1.59 (3)	-C(44)	1.48 (4)
-O(7)	2.04 (1)	-C(32)	1.54 (2)	-C(14)	1.55 (3)	-C(45)	1.40 (5)
-O(8)	2.01 (1)			-C(15)	1.59 (3)		
-O(7)′	2.47 (1)						

Bond Angles, Deg

Cr(1)-Cr(2)-O(7)′	167.4 (3)	C(13)-C(12)-C(14)	110 (2)	Cr(2)-Cr(1)-O(1)	89.4 (4)
O(1)-Cr(1)-O(2)	89.8 (5)	-C(15)	108 (2)	-O(2)	90.7 (4)
-O(3)	173.5 (5)	C(14)-C(12)-C(15)	115 (2)	-O(3)	84.0 (4)
-O(4)	87.7 (5)	C(21)-C(22)-C(23)	108 (2)	-O(4)	84.9 (4)
O(2)-Cr(1)-O(3)	90.7 (5)	-C(24)	111 (2)	-O(2)′	168.0 (3)
-O(4)	175.0 (5)	-C(25)	109 (2)	Cr(1)-Cr(2)-O(5)	85.4 (4)
O(3)-Cr(1)-O(4)	91.3 (5)	C(22)-C(23)-C(24)	111 (2)	-O(6)	84.5 (4)
O(5)-Cr(2)-O(6)	91.1 (5)	-C(25)	106 (2)	-O(7)	90.3 (4)
-O(7)	175.1 (5)	C(24)-C(23)-C(25)	112 (2)	-O(8)	89.8 (4)
-O(8)	87.6 (5)	C(31)-C(32)-C(33)	112 (1)	C(11)-C(12)-C(13)	108 (2)
O(6)-Cr(2)-O(7)	90.7 (5)	-C(34)	104 (1)	-C(14)	110 (2)
-O(8)	174.3 (5)	-C(35)	107 (1)	-C(15)	106 (2)
O(7)-Cr(2)-O(8)	90.2 (5)	C(33)-C(32)-C(34)	113 (1)	O(5)-C(11)-C(12)	114 (2)
Cr(1)-O(1)-C(11)	119 (1)	-C(35)	111 (1)	O(2)-C(21)-O(6)	126 (2)
Cr(2)-O(5)-C(11)	122 (1)	C(34)-C(32)-C(35)	109 (1)	-C(22)	118 (2)
Cr(1)-O(2)-C(21)	114 (1)	C(41)-C(42)-C(43)	107 (2)	O(6)-C(21)-C(22)	117 (2)
Cr(2)-O(6)-C(21)	124 (1)	-C(44)	105 (2)	O(3)-C(31)-O(7)	123 (2)
Cr(1)-O(3)-C(31)	126 (1)	-C(45)	108 (3)	-C(32)	118 (2)
Cr(2)-O(7)-C(31)	116 (1)	C(43)-C(42)-C(44)	104 (2)	O(7)-C(31)-C(32)	118 (2)
Cr(1)-O(4)-C(41)	122 (1)	-C(45)	115 (3)	O(4)-C(41)-O(8)	124 (2)
Cr(2)-O(8)-C(41)	118 (1)	C(44)-C(42)-C(45)	117 (3)	-C(42)	111 (2)
				O(8)-C(41)-C(42)	125 (2)

[a] Atoms are labeled as in Figure 4a. Primed atoms O(2)′ and O(7)′ are related to O(2) and O(7) by inversion.

units and isolated Cr^{2+} ions. The coordination polyhedron of the isolated Cr^{2+} ion is the expected tetragonally distorted octahedron. This is made up of trans weakly bound (Cr–O, 2.499 (2) Å) oxygen atoms that are part of the bridging formato groups in the $Cr_2(O_2CH)_4$ unit, trans water molecules (Cr–O, 2.063 (2) Å), and trans oxygen atoms of the formate ions that link Cr(1) to Cr(2) (Cr–O, 2.022 (2) Å).

The $Cr_2(O_2CH)_4$ unit in this compound has a crystallographic inversion center between the chromium atoms. The dimensions are such that full D_{4h} symmetry is closely approximated. It is interesting to note that the four short bonds to the Cr^{2+} ion have an average length, 2.04 Å, that differs but slightly from the average of the four Cr–O distances in the $Cr_2(O_2CH)_4$ unit, viz., 2.02 Å. The axial Cr–O distance in this compound, 2.224 Å, is the shortest yet observed in a $Cr_2(O_2CR)_4$ compound.

The structure is built of infinite chains of alternating monomer and dimer units. The chain extends in the $(\bar{x},y,z)$ direction, so that the singly primed atoms in Figure 1 can be generated from the doubly primed ones by a translation of $(\bar{1},1,1)$.

$Cr_2(O_2CH)_4(C_5H_5N)_2$ (II). This molecule[27] has a neat, crystallographically centrosymmetric structure,[28] and again, the actual dimensions within the $Cr_2(O_2CH)_4$ unit approximate very closely to the requirements of D_{4h} symmetry. The average of the Cr–O distances, 2.02 Å, is the same as in I, the other

Table V

(A) Positional and Thermal Parameters for $Cr_2(O_2CPh)_4(PhCO_2H)_2$ (V)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.0190 (1)	0.0960 (2)	−0.0166 (2)	0.00335 (7)	0.0048 (1)	0.0042 (1)	−0.0005 (2)	0.0005 (2)	−0.0009 (3)

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
O(1)	0.1399 (5)	0.0599 (6)	0.0443 (7)	3.2 (2)	C(22)	−0.0724 (7)	0.0839 (10)	0.354 (1)	3.2 (2)
O(2)	0.1047 (5)	−0.1214 (6)	0.0763 (7)	3.3 (2)	C(23)	−0.0463 (9)	0.1921 (11)	0.396 (1)	4.1 (3)
O(3)	−0.0166 (5)	0.1313 (6)	0.1555 (7)	3.0 (2)	C(24)	−0.0630 (9)	0.2235 (13)	0.520 (1)	5.1 (3)
O(4)	−0.0561 (5)	−0.0507 (6)	0.1895 (7)	3.2 (2)	C(25)	−0.1101 (10)	0.1459 (13)	0.592 (1)	5.6 (3)
O(5)	0.0612 (5)	0.2771 (7)	−0.0711 (8)	4.1 (2)	C(26)	−0.1384 (10)	0.0389 (13)	0.549 (1)	5.8 (4)
O(6)	0.1077 (6)	0.2521 (8)	−0.2630 (9)	5.5 (2)	C(27)	−0.1177 (10)	0.0074 (12)	0.426 (1)	4.6 (3)
C(11)	0.1594 (7)	−0.0377 (9)	0.081 (1)	2.5 (2)	C(31)	0.0967 (8)	0.3163 (11)	−0.162 (1)	3.8 (3)
C(12)	0.2469 (7)	−0.0619 (9)	0.136 (1)	2.5 (2)	C(32)	0.1266 (8)	0.4354 (10)	−0.176 (1)	3.2 (2)
C(13)	0.2695 (8)	−0.1727 (11)	0.173 (1)	4.0 (3)	C(33)	0.1676 (9)	0.4713 (11)	−0.283 (1)	4.7 (3)
C(14)	0.3509 (9)	−0.1917 (12)	0.235 (1)	4.8 (3)	C(34)	0.1952 (9)	0.5847 (13)	−0.292 (1)	5.4 (3)
C(15)	0.4059 (9)	−0.0987 (13)	0.256 (1)	5.2 (3)	C(35)	0.1825 (10)	0.6574 (13)	−0.191 (1)	5.5 (3)
C(16)	0.3836 (10)	0.0109 (13)	0.219 (1)	5.6 (4)	C(36)	0.1422 (9)	0.6205 (12)	−0.083 (1)	5.2 (3)
C(17)	0.3036 (8)	0.0307 (11)	0.156 (1)	3.9 (3)	C(37)	0.1151 (9)	0.5046 (11)	−0.074 (1)	4.1 (3)
C(21)	−0.0466 (7)	0.0537 (9)	0.225 (1)	2.6 (2)					

(B) Bond Distances and Angles in $Cr_2(O_2CPh)_4(HO_2CPh)_2$ (V)[a]

Bond Distances, A

Cr–Cr′	2.352 (3)	C(21)–O(3)	1.27 (1)	C(14)–C(15)	1.39 (1)	C(26)–C(27)	1.43 (2)
-O(1)	1.996 (6)	-O(4)	1.29 (1)	C(15)–C(16)	1.39 (1)	C(27)–C(22)	1.38 (1)
-O(2)′	2.010 (6)	-C(22)	1.51 (1)	C(16)–C(17)	1.41 (1)	C(32)–C(33)	1.40 (1)
-O(3)	1.994 (6)	C(31)–O(5)	1.22 (1)	C(17)–C(12)	1.40 (1)	C(33)–C(34)	1.40 (1)
-O(4)′	2.036 (6)	-O(6)	1.34 (1)	C(22)–C(23)	1.40 (1)	C(34)–C(35)	1.40 (2)
-O(5)	2.295 (7)	-C(32)	1.48 (1)	C(23)–C(24)	1.43 (1)	C(35)–C(36)	1.40 (1)
C(11)–O(1)	1.24 (1)	C(12)–C(13)	1.40 (1)	C(24)–C(25)	1.40 (2)	C(36)–C(37)	1.42 (1)
-O(2)	1.29 (1)	C(13)–C(14)	1.42 (1)	C(25)–C(26)	1.40 (2)	C(37)–C(32)	1.40 (1)
-C(1)	1.49 (1)						

Bond Angles, Deg

Cr′–Cr–O(1)	88.6 (2)	O(2)–C(11)–C(12)	116.5 (8)	C(21)–C(22)–C(23)	116.(1)
-O(2)′	87.6 (2)	O(3)–C(21)–O(4)	123.1 (8)	-C(27)	121 (1)
-O(3)	89.1 (2)	-C(22)	119.0 (8)	C(23)–C(22)–C(27)	123 (1)
-O(4)′	87.9 (2)	O(4)–C(21)–C(22)	117.9 (8)	C(22)–C(23)–C(24)	119 (1)
Cr′–Cr–O(5)	173.5 (2)	Cr(1)–O(5)–C(31)	133.2 (7)	C(23)–C(24)–C(25)	117 (1)
O(1)–Cr–O(2)′	176.2 (3)	O(5)–C(31)–O(6)	121 (1)	C(24)–C(25)–C(26)	124 (1)
-O(3)	89.7 (3)	-C(32)	125 (1)	C(25)–C(26)–C(27)	118 (1)
-O(4)′	89.1 (3)	O(6)–C(31)–C(32)	114 (1)	C(26)–C(27)–C(22)	119 (1)
O(2)′–Cr–O(3)	90.3 (3)	C(11)–C(12)–C(13)	120.6 (8)	C(31)–C(32)–C(33)	121 (1)
O(2)′–Cr–O(4)′	90.7 (3)	-C(17)	117.6 (8)	-C(37)	115 (1)
O(3)–Cr–O(4)′	176.8 (3)	C(13)–C(12)–C(17)	121.7 (9)	C(33)–C(32)–C(37)	124 (1)
Cr–O(1)–C(11)	121.0 (6)	C(12)–C(13)–C(14)	119 (1)	C(32)–C(33)–C(34)	119 (1)
Cr′–O(2)–C(11)	120.2 (6)	C(13)–C(14)–C(15)	119 (1)	C(33)–C(34)–C(35)	119 (1)
Cr–O(3)–C(21)	120.7 (6)	C(14)–C(15)–C(16)	122 (1)	C(34)–C(35)–C(36)	122 (1)
Cr′–O(4)–C(21)	119.2 (6)	C(15)–C(16)–C(17)	120 (1)	C(35)–C(36)–C(37)	119 (1)
O(1)–C(11)–O(2)	122.5 (8)	C(16)–C(17)–C(12)	118 (1)	C(36)–C(37)–C(32)	117 (1)
-C(12)	120.9 (8)				

[a] Atoms are labeled as in Figure 5.

$Cr_2(O_2CH)_4$ moiety described here.

$Cr_2(O_2CCF_3)_4(Et_2O)_2$ (III). As with I, we have a single, crystallographically centrosymmetric molecule[29] in the unit cell, and again, as in I and II, the structure comes very close to having D_{4h} symmetry. The average of the Cr–O distances, 2.015 Å, is not significantly different from those in I and II. This compound has the longest Cr–Cr distance yet observed, 2.541 (1) Å, in compounds of the $Cr_2(O_2CR)_4L_2$ type.

$Cr_2(O_2CCMe_3)_4$ (IV). This compound is isomorphous with its molybdenum analogue.[4] The entire molecule constitutes the asymmetric unit, and no crystallographic symmetry is imposed on it. In the absence of any discrete axial ligands, the molecules are arranged in infinite chains (Figure 4b) so that the axial positions on each molecule are filled, at distances 2.44 and 2.47 Å, by oxygen atoms of its neighbors. This is the same general arrangement found in $Cr_2(O_2CCH_3)_4$, $Mo_2(O_2CCH_3)_4$, and $CrMo(O_2CCH_3)_4$.[4] The bulky CMe_3 groups do, apparently, cause the axial intermolecular contacts to be much longer than those (2.327 Å) in the acetate, which was the objective in studying this compound. In this case, the approach to D_{4h} symmetry in the $Cr_2(O_2CCMe_3)_4$ unit is not as close as in the preceding cases; this is particularly evident in the variation in the Cr–Cr–O angles, which range from 84.0° to 90.7°. Presumably, however, these distortions result from the packing and isolated molecules would be more symmetrical.

It is interesting to note that the mean Cr–O distance here is 2.02 Å, which is not significantly different from that in the trifluoroacetate, even though these two molecules contain the most electronically diverse R groups in the carboxylate anions.

$Cr_2(O_2CPh)_4(PhCO_2H)_2$ (V). The structure is made up of centrosymmetric molecules packed at van der Waals distances. The $Cr_2(O_2C)_4$ core of the molecule deviates but little from D_{4h} symmetry, and the mean Cr–O distance is 2.01 Å.

The C(31)–O(5) distance, 1.22 (1) Å, shows that it is the C=O oxygen atom of benzoic acid that is coordinated to Cr in the axial positions.

Cr_2(9-anthracenecarboxylate)$_4$DME (VI). This compound was prepared and studied in the hope that the anthracenyl R groups might cause the molecules to pack with extremely long

Table VI

(A) Positional and Thermal Parameters for $Cr_2(O_2CC_{14}H_9)_4DME$ (VI)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr(1)	−0.0010 (1)	0.0170 (1)	0.1251 (2)	0.00221 (5)	0.00193 (5)	0.0069 (2)	0.0005 (1)	0.0026 (2)	0.0004 (2)
O(1)	−0.1028 (4)	0.0712 (4)	0.0728 (7)	0.0021 (2)	0.0034 (3)	0.0059 (9)	0.0015 (5)	0.0009 (8)	0.0000 (9)
O(2)	0.0533 (4)	0.1221 (4)	0.0853 (8)	0.0027 (3)	0.0031 (3)	0.0053 (9)	−0.0010 (5)	0.0006 (8)	−0.0008 (9)
O(3)	−0.1013 (4)	0.0372 (4)	−0.1694 (8)	0.0018 (2)	0.0027 (3)	0.0085 (10)	0.0013 (4)	0.0005 (8)	−0.0016 (9)
O(4)	0.0511 (4)	0.0900 (4)	−0.1609 (8)	0.0019 (2)	0.0024 (3)	0.0083 (10)	−0.0004 (5)	0.0014 (8)	0.0013 (9)
O(5)	−0.0097 (5)	0.0550 (6)	0.3719 (9)	0.0050 (4)	0.0052 (4)	0.0070 (10)	−0.0010 (7)	−0.0003 (11)	0.0032 (12)

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
C(1)	−0.1295 (5)	0.0727 (6)	−0.063 (1)	2.1 (2)	C(17)	0.1169 (6)	0.2124 (7)	−0.075 (1)	3.0 (2)
C(2)	−0.1979 (6)	0.1290 (6)	−0.102 (1)	2.4 (2)	C(18)	0.1822 (7)	0.2072 (7)	−0.160 (1)	3.4 (2)
C(3)	−0.2694 (7)	0.1136 (7)	−0.044 (1)	3.2 (2)	C(19)	0.2011 (7)	0.1354 (8)	−0.238 (2)	4.3 (3)
C(4)	−0.2830 (7)	0.0407 (7)	0.040 (1)	3.9 (3)	C(20)	0.2639 (8)	0.1330 (9)	−0.324 (2)	5.3 (3)
C(5)	−0.3512 (8)	0.0272 (8)	0.098 (2)	4.5 (3)	C(21)	0.3125 (9)	0.2043 (9)	−0.330 (2)	5.7 (3)
C(6)	−0.4146 (8)	0.0862 (9)	0.070 (2)	4.8 (3)	C(22)	0.2971 (8)	0.2730 (9)	−0.252 (2)	5.2 (3)
C(7)	−0.4029 (8)	0.1570 (9)	−0.007 (2)	5.4 (3)	C(23)	0.2303 (7)	0.2774 (8)	−0.167 (1)	4.0 (3)
C(8)	−0.3293 (7)	0.1722 (8)	−0.069 (1)	3.8 (3)	C(24)	0.2139 (8)	0.3499 (9)	−0.092 (2)	4.9 (3)
C(9)	−0.3177 (7)	0.2442 (8)	−0.153 (1)	4.0 (3)	C(25)	0.1476 (7)	0.3561 (8)	−0.013 (1)	3.9 (3)
C(10)	−0.2474 (6)	0.2584 (7)	−0.206 (1)	3.4 (2)	C(26)	0.1273 (9)	0.4329 (10)	0.056 (2)	6.0 (4)
C(11)	−0.2335 (9)	0.3359 (9)	−0.282 (2)	5.7 (3)	C(27)	0.0647 (9)	0.4393 (10)	0.132 (2)	6.1 (4)
C(12)	−0.1632 (9)	0.3520 (10)	−0.331 (2)	6.0 (4)	C(28)	0.0123 (8)	0.3743 (9)	0.137 (2)	5.0 (3)
C(13)	−0.1020 (8)	0.2952 (9)	−0.306 (2)	5.4 (3)	C(29)	0.0286 (7)	0.2980 (8)	0.075 (1)	4.0 (3)
C(14)	−0.1138 (7)	0.2222 (7)	−0.236 (1)	3.4 (2)	C(30)	0.0978 (6)	0.2867 (7)	−0.003 (1)	3.0 (2)
C(15)	−0.1852 (6)	0.2016 (7)	−0.181 (1)	2.7 (2)	C(31)	−0.0812 (13)	0.0444 (14)	0.447 (3)	10.0 (6)
C(16)	0.0714 (6)	0.1374 (7)	−0.046 (1)	2.7 (2)	C(32)	0.0598 (18)	0.0646 (21)	0.470 (4)	16.4 (10)

(B) Bond Distances and Angles in $Cr_2(O_2CC_{14}H_9)_4(DME)$ (VI)[a]

Bond Distances, Å

Cr(1)–Cr(1)′	2.283 (2)	O(1)–O(3)	2.213 (6)	C(12)–C(11)	1.36 (1)	C(24)–C(23)	1.40 (1)
Cr(1)–O(1)	2.011 (4)	O(2)–O(4)	2.235 (6)	–C(13)	1.42 (1)	–C(25)	1.41 (1)
–O(2)	2.009 (5)	C(3)–C(2)	1.41 (1)	C(14)–C(13)	1.37 (1)	C(25)–C(26)	1.45 (1)
–O(3)′	2.009 (4)	–C(4)	1.44 (1)	–C(15)	1.42 (1)	–C(30)	1.44 (1)
–O(4)′	1.993 (4)	–C(8)	1.43 (1)	C(15)–C(2)	1.41 (1)	C(27)–C(26)	1.33 (1)
–O(5)	2.283 (5)	C(5)–C(4)	1.35 (1)	C(18)–C(17)	1.42 (1)	–C(28)	1.41 (1)
C(1)–O(1)	1.257 (7)	–C(6)	1.48 (1)	–C(19)	1.41 (1)	C(29)–C(28)	1.40 (1)
–O(3)	1.237 (7)	C(7)–C(6)	1.37 (1)	–C(23)	1.43 (1)	–C(30)	1.45 (1)
–C(2)	1.527 (9)	–C(8)	1.46 (1)	C(20)–C(19)	1.39 (1)	C(30)–C(17)	1.42 (1)
C(16)–O(2)	1.253 (8)	C(9)–C(8)	1.41 (1)	–C(21)	1.45 (1)	O(5)–C(31)	1.47 (1)
–O(4)	1.303 (8)	–C(10)	1.37 (1)	C(22)–C(21)	1.36 (1)	–C(32)	1.45 (2)
–C(17)	1.494 (10)	C(10)–C(11)	1.46 (1)	–C(23)	1.44 (1)	C(31)–C(32)′	1.95 (3)
		–C(15)	1.43 (1)				

Bond Angles, Deg

Cr(1)′–Cr(1)–O(1)	88.0 (1)	C(31)–O(5)–C(32)	117 (1)	C(16)–C(17)–C(18)	120.1 (6)
–O(2)	89.8 (1)	O(5)–C(31)–C(32)′	98 (1)	–C(30)	118.8 (6)
–O(3)′	90.0 (1)	O(5)–C(32)–C(31)′	105 (1)	C(18)–C(17)–C(30)	120.9 (7)
–O(4)′	88.9 (1)	C(1)–C(2)–C(3)	120.9 (6)	C(17)–C(18)–C(19)	122.4 (7)
Cr(1)′–Cr(1)–O(5)	176.7 (2)	–C(15)	118.0 (6)	–C(23)	118.5 (7)
O(1)–Cr(1)–O(2)	90.3 (2)	C(3)–C(2)–C(15)	120.7 (6)	C(19)–C(18)–C(23)	119.1 (7)
–O(3)′	177.9 (2)	C(2)–C(3)–C(4)	121.6 (7)	C(18)–C(19)–C(20)	121.1 (8)
–O(4)′	91.8 (2)	–C(8)	119.0 (7)	C(19)–C(20)–C(21)	119.6 (9)
O(2)–Cr(1)–O(3)′	89.1 (2)	C(4)–C(3)–C(8)	119.4 (7)	C(20)–C(21)–C(22)	120.5 (9)
–O(4)′	177.4 (2)	C(3)–C(4)–C(5)	121.2 (7)	C(21)–C(22)–C(23)	120.5 (9)
O(3)′–Cr(1)–O(4)′	90.1 (2)	C(4)–C(5)–C(6)	120.4 (8)	C(18)–C(23)–C(22)	119.2 (7)
Cr(1)–O(1)–C(1)	119.0 (4)	C(5)–C(6)–C(7)	119.8 (8)	–C(24)	121.2 (8)
Cr(1)′–O(3)–C(1)	117.5 (4)	C(6)–C(7)–C(8)	120.1 (8)	C(22)–C(23)–C(24)	119.6 (8)
Cr(1)–O(2)–C(16)	119.4 (4)	C(3)–C(8)–C(7)	119.0 (7)	C(23)–C(24)–C(25)	120.3 (8)
Cr(1)′–O(4)–C(16)	119.8 (4)	–C(9)	120.7 (7)	C(24)–C(25)–C(26)	120.6 (8)
O(1)–C(1)–O(3)	125.1 (6)	C(7)–C(8)–C(9)	120.3 (8)	–C(30)	119.9 (7)
–C(2)	116.8 (6)	C(8)–C(9)–C(10)	119.3 (7)	C(26)–C(25)–C(30)	119.4 (7)
O(3)–C(1)–C(2)	117.9 (6)	C(9)–C(10)–C(11)	119.3 (7)	C(25)–C(26)–C(27)	121.0 (9)
O(2)–C(16)–O(4)	121.9 (6)	–C(15)	121.8 (7)	C(26)–C(27)–C(28)	121.3 (10)
–C(17)	119.8 (6)	C(11)–C(10)–C(15)	118.8 (7)	C(27)–C(28)–C(29)	120.6 (9)
O(4)–C(16)–C(17)	118.3 (6)	C(10)–C(11)–C(12)	119.9 (9)	C(28)–C(29)–C(30)	120.1 (7)
O(5)–Cr(1)–O(1)	88.7 (2)	C(12)–C(13)–C(14)	120.2 (9)	C(17)–C(30)–C(25)	119.1 (7)
–O(2)	90.1 (2)	C(11)–C(12)–C(13)	120.9 (10)	–C(29)	123.6 (7)
–O(3)′	93.3 (2)	C(13)–C(14)–C(15)	122.0 (7)	C(25)–C(30)–C(29)	117.3 (7)
–O(4)′	91.4 (2)	C(2)–C(15)–C(10)	118.6 (6)		
Cr(1)–O(5)–C(31)	121.3 (7)	–C(14)	123.3 (6)		
–C(32)	119.2 (9)	C(14)–C(15)–C(10)	118.1 (6)		

[a] Atoms are labeled as in Figure 6a.

axial contacts. This hope was, of course, frustrated by the fact that these groups twist so that they are not parallel to the Cr–Cr axis, thus leaving room in the axial positions for the inclusion of the bidentate $MeOCH_2CH_2OMe$ groups.

The structure of the molecule is best appreciated in the stereoscopic presentation, Figure 6b. There is a crystallo-

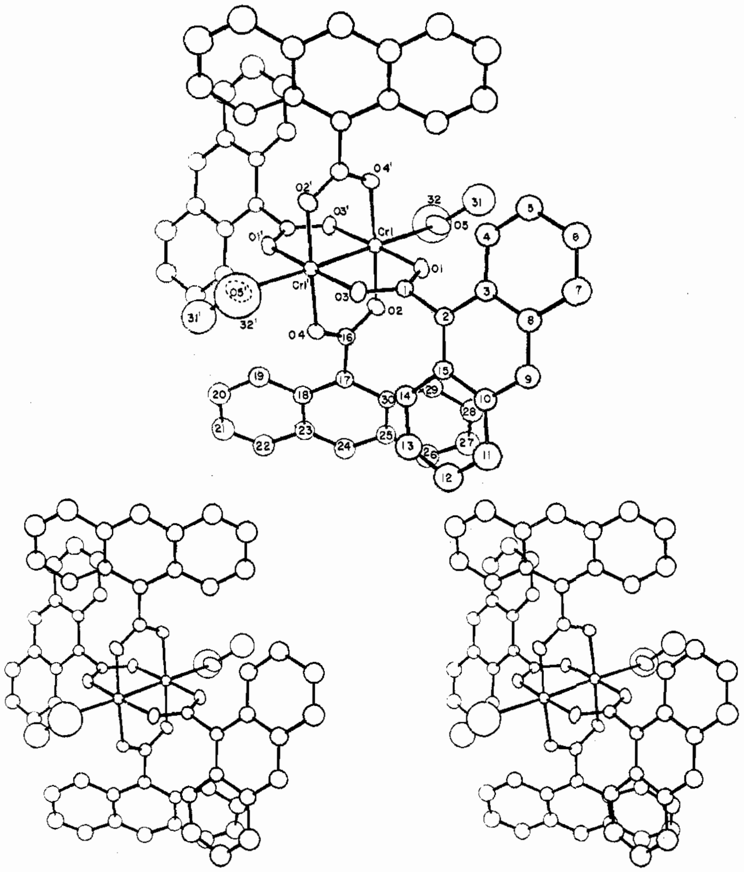

Figure 6. (a, top) An ORTEP of the Cr_2(9-anthracenecarboxylate)$_4$DME (VI) molecule showing the atom labeling scheme and using 33% probability ellipsoids. The molecule possesses C_i symmetry; primed and unprimed atoms are related by the inversion center. Only half of the disordered DME molecule is shown. (b, bottom) A stereoview of the Cr_2(9-anthracenecarboxylate)$_4$(DME) molecule using the same molecular orientation as seen in Figure 6a.

graphic center of symmetry, and the deviations from D_{4h} symmetry are minor.

This molecule nominally has the smallest Cr–Cr distance so far reported in a $Cr_2(O_2CR)_4L_2$-type compound, although there is no statistically significant difference between the value of 2.283 (2) Å found here and 2.288 (1) Å found in the anhydrous acetate.

Discussion

In an earlier report[14] from this laboratory, it was shown that $Cr_2(O_2CCH_3)_4$, in which there are intermolecular axial interactions (Cr··O, 2.327 (4) Å), has a significantly shorter Cr–Cr bond, 2.288 (2) Å, than that found in $Cr_2(O_2CCH_3)_4(H_2O)_2$, 2.362 (1) Å, where there are more closely bound axial water molecules (Cr···O, 2.272 Å). The inverse relationship between the Cr–Cr and Cr–L_{axial} distances was noted, and it was argued that such an inverse correlation should be more general. It is also reasonable to suppose that the Cr–Cr distance might depend on the inductive effect of the R group in the carboxylate ligand, RCO_2^-. The simplest model that might incorporate both of these dependences would be that which assumes that the Cr–Cr distance is a linear function of each parameter and that the two parameters exert their influences independently. We shall call this the independent, linear model. In algebraic form it can be expressed as

$$d_{Cr-Cr} = f(d_{Cr-L_{axial}})^{-1} + f'(IE_R)$$

It is possible to vary the R group quite deliberately by choosing the carboxylic acid, but control over the presence or absence of axial ligands, and their distance from the chromium atoms, cannot be achieved in any systematic way. Thus, the first six compounds we have examined do not provide enough data for a completely definitive picture of how Cr–Cr bond lengths depend on the two variables. These data are sufficient to test the validity of the independent, linear, two-parameter model.

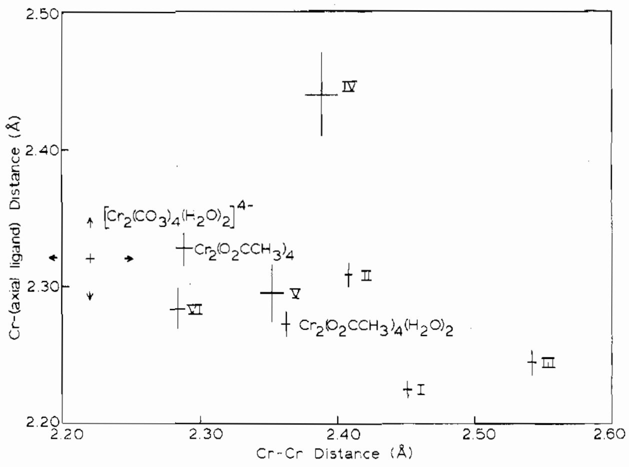

Figure 7. A plot of the Cr–Cr bond distances vs. the Cr–L_{axial} distances for six $Cr_2(O_2CR)_4L_2$ compounds and $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$. The six compounds whose structures are reported here for the first time are identified by the numbers I–VI. Error limits shown correspond to 3σ. For the carbonato species, no ESD's were reported, and the error limits are estimates based on the apparent accuracy of the structure.

The Cr–Cr and Cr–L_{axial} distances for the six compounds whose structures are reported here, as well as data for the hydrated[12] and anhydrous[14] acetates, are plotted in Figure 7. The point for the $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$ ion[13] is also shown,

Table VII. Crystallographic Data

Parameter	I	II	III	IV	V	VI
Formula	$Cr_3(O_2CH)_6$-$(H_2O)_2$	$Cr_2(O_2CH)_4$-$(C_5H_5N)_2$	$Cr_2(O_2CCF_3)_4$-$[O(C_2H_5)_2]_2$	$Cr_2(O_2CCMe_3)_4$	$Cr_2(O_2CPh)_4$-$(HO_2CPh)_2$	$Cr_2(O_2CAn)_4$-(DME)
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Å	7.009 (1)	10.220 (2)	9.408 (2)	11.647 (2)	15.252 (3)	17.500 (4)
b, Å	8.734 (2)	11.175 (2)	9.954 (2)	11.993 (3)	11.709 (3)	16.362 (3)
c, Å	6.838 (1)	7.739 (1)	8.590 (1)	10.082 (2)	10.847 (2)	8.835 (1)
α, deg	111.52 (1)	90	91.31 (1)	90.45 (2)	90	90
β, deg	91.40 (1)	96.48 (1)	102.85 (1)	105.28 (2)	90.70 (2)	94.44 (1)
γ, deg	68.55 (2)	90	66.12 (1)	71.11 (2)	90	90
V, Å^3	359.5 (1)	878.3 (4)	715.1 (3)	1281.1 (5)	1936.9 (6)	2522.3 (8)
d_X, g/cm^3	2.13	1.67	1.64	1.319	1.428	1.421
Z	1	2	1	2	2	2
Formula wt	462.13	442.27	704.30	508.5	832.7	1079.1
Crystal size, mm	0.3 × 0.3 × 0.7	0.25 × 0.5 × 0.5	0.2 × 0.5 × 0.5	0.12 × 0.14 × 0.36	0.2 × 0.3 × 0.5	0.59 × 0.32 × 0.34
μ, cm^{-1}	23.95	13.36	9.23	9.24	6.53	5.19
Range of 2θ, deg	0–50	0–50	0–50	0–45	0–45	0–48
No. of unique data	1282	1540	2348	3371	2540	3954
No. of data, $F_o^2 > 3\sigma(F_o^2)$	1086	1210	1786	1207	1184	2338
No. of variables	106	118	181	131	118	183
R_1	0.035	0.044	0.049	0.093	0.074	0.106
R_2	0.054	0.065	0.070	0.117	0.088	0.140
ESD	1.370	1.521	1.593	2.034	1.578	2.669
Largest peak, e/Å^3	1.14	1.15	1.42	1.71	0.59	1.25

although the implication that this species ought to be grouped with the carboxylates is not one that we would insist on.

It is immediately evident from the overview of all the data that each of the structural features we are dealing with spans a formidable range. Most interesting, perhaps, is the great range of Cr–Cr distances. While the majority of them lie between 2.28 and 2.45 Å, the known outer limits are now defined by the carbonato bridged species at 2.22 Å and the CF_3CO_2 bridged molecule at 2.54 Å. In a very general sort of way, these results are in line with the recent theoretical work of Benard and Veillard,[18] who calculated a very broad, shallow potential-energy curve having a minimum near 2.4 Å.

The data now available indicate that there is a more general inverse correlation between the two distances, but not a close or quantitative one. If one omits the point for compound IV, the remaining points, though scattered, do suggest a line or curve that is qualitatively of the correct form (i.e., negative slope as plotted). Also, on comparing pairs of compounds with the same R but different axial ligand distances, the inverse relationship is observed both for the acetates and the formates (I and II), although the slopes of the lines connecting these pairs may be somewhat different. It must be admitted that the relationship of the points for V and VI is not that expected on the assumption that, though the R groups in these two compounds are not actually identical, they must surely be rather similar electronically. However, this comparison may not be justified because in V each phenyl groups is very nearly coplanar with its CO_2 group (dihedral angles of 8 and 12° for the two crystallographically independent ligands) while the anthracenyl groups in VI are turned through rather large angles (45 and 69°).

The fact that the slopes of the lines connecting the points for the two acetato and the two formato compounds may not be parallel indicates by itself that a simple dependence of d_{Cr-Cr} on $(d_{Cr-L_{axial}})^{-1}$, independent of any other parameters, is probably not a valid assumption. The available data also invalidate the idea of a simple dependence of d_{Cr-Cr} on the inductive effect of R. The fact that the point for IV is far from the best line through the others would have to be explained on the linear, independent, two-parameter model by invoking an inductive effect. This would have to operate in the sense that the greater the inductive effect of R, the longer is the Cr–Cr bond. However, this ad hoc assumption for the pivalate is inconsistent with the fact that the point for the trifluoroacetate, III, is more or less in line with the other compounds instead of being much further to the left.

We conclude that the available data for the six $Cr_2(O_2CR)_4L_2$ compounds (as well as the carbonato anion) invalidate the simple idea that d_{Cr-Cr} depends linearly and independently on the $Cr-L_{axial}$ bond length and the inductive effect of the R group. We are not prepared to suggest what additional considerations must be invoked to correlate the data. Indeed, it appears that the available data are insufficiently systematic to allow the construction of a consistent model. We intend to examine more compounds with a view to developing a broader and more systematic data base.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. I, 64611-48-9; II, 64626-97-7; III, 15684-01-2; IV (salt form), 64611-49-0; IV (complex form), 64653-26-5; V (salt form), 64611-50-3; V (complex form), 64626-96-6; VI, 64626-95-5; $(NH_4)_4(Cr_2(CO_3)_4(H_2O)_3)$, 31276-88-7; Cp_2Cr, 1271-24-5.

Supplementary Material Available: Final calculated and observed structure factors (41 pages). Ordering information is given on any current masthead page.

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(23) We are grateful to Professor M. H. Chisholm for suggesting to us the utility of Cp_2Cr as a starting material for the preparation of these and other compounds of divalent chromium.
(24) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organomet. Chem.*, **50**, 227 (1973).
(25) The Enraf-Nonius structure determination package was used on a PDP 11/45 computer at the Molecular Structure Corporation, College Station, Texas. The structure factors and anomalous dispersion corrections were taken from sources previously cited.[14]
(26) This is presumably the same compound formulated by Herzog and Kalies[21] as $Cr(O_2CH)_2(H_2O)$, the difference being only $^1/_3$ H_2O/Cr. They reported a magnetic moment, μ_{eff}, at room temperature, per Cr atom of 1.35, which is considerably higher than the moments of ca. 0.5 commonly reported for compounds containing Cr only in $Cr_2(O_2CR)_4$ units. This higher value is now qualitatively understandable because of the presence of the isolated Cr(II) ions. It is not clear what significance is to be attached to it quantitatively. An approximate μ_{eff} for the isolated Cr(II) ion may be calculated as $3^{1/2} \times 1.35 = 2.34$, which is too low even for an isolated spin triplet (≥2.83) Cr(II) ion, let alone a spin quintet (≥4.89).
(27) The first report of this compound seems to be that of W. Traube, E. Burmeister, and R. Stahn, *Z. Anorg. Allg. Chem.*, **147**, 50 (1925). Herzog and Kalies, *ibid.*, **351**, 237 (1967), report some other $Cr_2(O_2CH)_4$-(N-ligand)$_2$ compounds, all of which appear to be magnetically normal for dimers.
(28) It may be noted that the two Cr-Cr vectors per unit cell lie at an angle of 26.4° to each other, thus making this substance a possible candidate for study of spectral polarizations.
(29) Since there is only one molecule per unit cell, all Cr-Cr vectors are parallel. In agreement with this, the crystals are extremely dichroic; they are generally purple, but virtually colorless in one orientation when viewed in polarized light.

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Preparation and Structure of a Quadruply Bonded Dimolybdenum Compound Containing the 7-Azaindolyl Ligand

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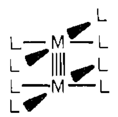
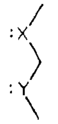
The reaction of 7-azaindole with $Mo_2Cl_4(PEt_3)_4$ gives a 29% yield of emerald green $Mo_2Cl_2(PEt_3)_2(C_7H_5N_2)_2$. The compound has been characterized by x-ray crystallography. It crystallizes in space group $P2_1/n$ with $a = 16.077$ (5) Å, $b = 8.936$ (2) Å, $c = 10.976$ (2) Å, $\beta = 94.52$ (2)°, $V = 1571.8$ (6) Å^3, and $Z = 2$. The molecules lie on crystallographic inversion centers, and the ligand arrangement is such that there is no additional molecular symmetry possible. Thus, the $Mo_2P_2Cl_2$ atoms are coplanar and the two azaindolyl groups lie above and below this plane oriented in opposite directions. The Mo-Mo distance is 2.125 (1) Å and all other distances are normal. There is some disorder in the PEt_3 group.

Introduction

The size (i.e., M-M distances usually in the range 2.0-2.4 Å) and square-prismatic geometry (idealized D_{4h} symmetry with M-M-L angles of 90-105°) of typical quadruply bonded dimetal units, I, result in their having a stereochemical preference for ligands of the class represented schematically by II in which the donor atoms X and Y are separated by ca. 2.2 Å and the axes of their donor orbitals are aligned approximately parallel. The number of potential ligands in this class is very large; those which have already been shown crystallographically to occur in complexes of M-M quadruply bonded units are shown in Chart I.

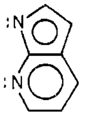


I

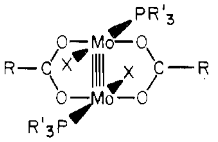


II

We describe here a compound containing the dinitrogen, monoanionic ligand 7-azaindolyl, III. The compound is unusual in another respect. There have been only a few compounds reported in which as many as three different kinds of ligands, including one of type II, are present. These are the compounds of type IV, prepared by San Filippo and Sniadoch,[8] one of which (R = C_6H_5, R′ = n-C_4H_9, X = Br) was structurally characterized by Potenza, Johnson, and San Filippo.[9] The compound we report here is analogous except that the carboxylato groups are replaced by III, the 7-azaindolyl group.

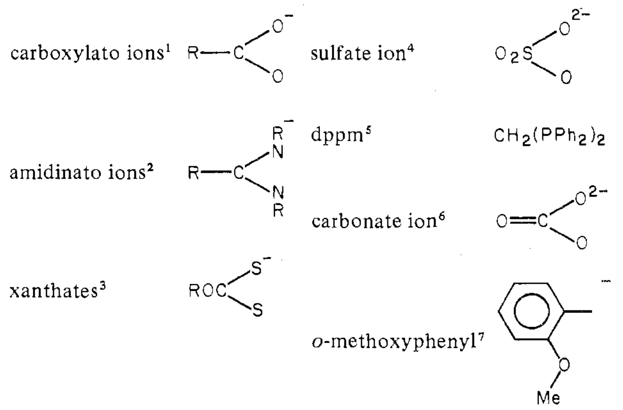


III



IV

Chart I



Experimental Section

Preparation. The entire procedure is carried out under anaerobic conditions with dry, degassed solvents. A mixture of 0.50 g (4.24 mmol) of 7-azaindole and 1.71 g (2.12 mmol) of $Mo_2Cl_4(PEt_3)_4$[10] in 50 mL of benzene was heated at reflux for 2 h, cooled to room temperature, and then filtered to give 0.45 g (0.61 mmol) of an emerald green crystalline product. Large black acicular crystals were obtained by slow recrystallization of the product from hot toluene.

X-Ray Structural Characterization. Data Collection. A crystal measuring 0.45 × 0.32 × 0.27 mm was mounted in a sealed glass

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