

The Crystal and Molecular Structures of Dichromium Tetra-Acetate Dihydrate and Dirhodium Tetra-Acetate Dihydrate

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(Received 27 August 1970)

Single-crystal X-ray diffraction results are given for chromous acetate, $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$, and for rhodium acetate, $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$. Both crystals conform to space group $C2/c$ with $a = 13.287 \pm 0.013$, $b = 8.608 \pm 0.009$, $c = 14.042 \pm 0.015$ Å, $\beta = 117^\circ 14' \pm 3'$, $\rho_{\text{meas}} = 2.23$ g.cm $^{-3}$, $\rho_{\text{calc}} = 2.24$ g.cm $^{-3}$ in the case of rhodium acetate and $a = 13.211 \pm 0.006$, $b = 8.617 \pm 0.003$, $c = 13.962 \pm 0.005$ Å, $\beta = 116^\circ 51' \pm 2'$, $\rho_{\text{meas}} = 1.79$ g.cm $^{-3}$, $\rho_{\text{calc}} = 1.762$ g.cm $^{-3}$ for the chromous acetate. Both data sets were collected by counter methods and were refined by full-matrix least-squares methods to conventional R values of 2.7% (rhodium acetate) and 3.4% (chromous acetate). The coordination around both metals is essentially octahedral and the Rh–Rh and Cr–Cr distances [2.3855 (5) and 2.362 (1), respectively] in these carboxylato-bridged dimers imply multiple (as opposed to single) metal-metal bonds. There is evidence of some hydrogen bonding between water hydrogen atoms and acetate oxygen atoms in neighboring molecules.

Introduction

The structures of binuclear carboxylato-bridged transition metal compounds are of interest because the carboxylates provide a framework within which a wide range of metal-metal interactions may occur, depending on the nature of the metal atoms concerned. The structures of the acetates of copper(II) (van Niekerk & Schoening, 1953), chromium(II) (van Niekerk, Schoening & de Wet, 1953), molybdenum(II) (Lawton & Mason, 1965), rhodium(II) (Porai-Koshits & Antschishkina, 1962) and rhenium(III) (Bennett, Bratton, Cotton & Robinson, 1968) have all been studied and for the heavier metals a significant amount of metal-metal bonding is indicated by the short M–M distances. The reported Cr–Cr bond distance of 2.64 Å in $[\text{Cr}(\text{O}_2\text{CCH}_3)_2 \cdot \text{H}_2\text{O}]_2$ has been taken (Figgis & Martin, 1956; Cotton, 1967) as evidence of very weak Cr–Cr interaction. Since the compound is diamagnetic, such an extremely weak interaction is suspect, and since the reported distance appears to be based mainly on anal-

ogy with the corresponding copper compound, the structure was re-investigated.

The accuracy of the distance (2.45 Å) reported for the Rh–Rh bond in rhodium acetate, $[\text{Rh}(\text{O}_2\text{CCH}_3)_2 \cdot \text{H}_2\text{O}]_2$ is also questionable since this distance appears to be based on Patterson projections alone. Because the nature of this metal-metal bond is important in comparing it with those in related compounds, an accurate structural study was carried out.

Procedure

Anhydrous rhodium acetate was prepared by standard methods (Rempel, Legzdins, Smith & Wilkinson, 1971). Blue-green single crystals of $[\text{Rh}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}]_2$ suitable for X-ray work were obtained by precipitation of $[\text{Rh}(\text{CH}_3\text{CO}_2)_2]_2$ from aqueous solution. A diamond-shaped plate (diamond diagonals 0.282×0.237 mm, thickness 0.127 mm) mounted on a glass fiber was used for all subsequent work. Precession films of $h0l$; $h1l$; h , $k-h$, $2h$; and $h+2$, $k-h$, $2h+1$ showed the crystal

Table 1. Atomic coordinates for $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$

	x	y	z	$B(\text{Å}^2)$
Rh	0.04467 (2)	0.07453 (2)	−0.04161 (2)	
O(5)	0.1243 (2)	0.2109 (3)	−0.1319 (2)	
O(3)	−0.0971 (2)	0.1291 (3)	0.0781 (2)	
C(3)	−0.0680 (2)	0.2566 (4)	0.0525 (2)	
O(4)	−0.0115 (2)	0.2692 (2)	0.0005 (2)	
O(2)	0.1021 (2)	−0.0575 (2)	0.1812 (2)	
C(1)	0.1842 (2)	0.0223 (4)	0.1844 (2)	
O(1)	0.1853 (2)	0.0873 (2)	0.1041 (2)	
C(4)	−0.1051 (4)	0.4037 (4)	0.0845 (4)	
C(2)	0.2858 (3)	0.0397 (6)	0.2912 (3)	
H(41)	−0.073 (5)	0.408 (6)	0.160 (5)	6.4 (1.3)
H(42)	−0.067 (4)	0.504 (8)	0.086 (5)	6.3 (1.1)
H(43)	−0.180 (6)	0.419 (6)	0.039 (6)	6.9 (1.4)
H(22)	0.346 (5)	0.130 (8)	0.297 (5)	7.2 (1.3)
H(23)	0.320 (6)	−0.061 (8)	0.328 (7)	8.8 (1.9)
H(21)	0.259 (7)	0.070 (8)	0.338 (7)	8.7 (2.0)

Table 2. *Thermal parameters* (\AA^2) for $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	1.32 (1)	1.51 (1)	1.37 (1)	-0.15 (1)	0.72 (1)	-0.03 (1)
O(3)	2.52 (9)	2.28 (9)	2.94 (10)	-0.04 (7)	1.71 (8)	-0.42 (8)
O(4)	2.62 (8)	1.72 (8)	2.80 (9)	0.09 (7)	1.52 (8)	-0.06 (8)
O(1)	1.71 (8)	2.73 (10)	1.97 (8)	-0.43 (7)	0.68 (7)	-0.06 (7)
O(2)	1.97 (8)	2.92 (10)	1.64 (8)	-0.43 (6)	0.55 (7)	0.17 (7)
O(5)	4.45 (11)	3.67 (11)	3.27 (10)	-1.78 (10)	2.82 (10)	-0.87 (10)
C(3)	1.77 (10)	2.01 (12)	2.03 (12)	0.37 (9)	0.54 (9)	-0.35 (9)
C(4)	3.20 (16)	2.32 (15)	3.87 (19)	0.46 (12)	1.67 (15)	-0.85 (13)
C(1)	1.88 (10)	2.03 (11)	1.77 (11)	-0.04 (9)	0.65 (9)	-0.05 (10)
C(2)	2.63 (15)	5.40 (14)	2.10 (14)	-1.16 (15)	0.22 (12)	0.32 (15)

to be monoclinic with systematic absences on hkl for $h+k=2n+1$ and on $h0l$ for $l=2n+1$ conforming to the space groups $C2/c$ or Cc . Unit-cell dimensions were measured and the data were collected at $21 \pm 1^\circ\text{C}$ using Zr-filtered $\text{Mo } K\alpha$ radiation ($\lambda=0.7107 \text{\AA}$). The following unit-cell dimensions were obtained from a least-squares refinement of the setting angles of 30 reflections that had been carefully centered on a General Electric XRD-5 manual diffractometer: $a=13.287 \pm 0.013$, $b=8.608 \pm 0.009$, $c=14.042 \pm 0.015 \text{\AA}$, $\beta=117^\circ 14' \pm 3'$. The density, measured by flotation in a mixture of CCl_4 and CH_2I_2 , is $2.23 \pm 0.08 \text{ g.cm}^{-3}$. With four dinuclear molecules per unit cell the density calculated from the formula weight of 478.021 and the unit-cell volume of 1427.93\AA^3 is 2.24 g.cm^{-3} .

Hydrated chromium(II) acetate was prepared by a standard method (Brauer, 1965). Analysis for $\text{C}_4\text{H}_8\text{O}_5\text{Cr}$: calculated: Cr, 27.65; C, 25.54; H, 4.28; found: Cr, 27.1; C, 26.1; H, 4.26. Crystals suitable for X-ray work were grown at *ca.* 25° over a period of several days from an air-free saturated aqueous solution. The crystals were purified by reflected light and red by transmitted light. A somewhat irregular but roughly cylindrical crystal 0.18 mm in diameter by 0.35 mm in length was placed in a capillary and used for all subsequent work. Weissenberg and oscillation photographs showed that the crystal was mounted along the $[110]$ direction and had d spacings in good agreement with expectation from the unit-cell dimensions reported by van Niekerk *et al.* (1953). The crystal was then transferred to the diffractometer and the a^* , b^* and c^* axes were located. Unit-cell dimensions were measured and intensity data were collected at $22 \pm 1^\circ$ using zirconium-filtered $\text{Mo } K\alpha$ radiation. From a least-squares refinement of the setting angles of 23 reflections that had been carefully centered, the following unit-cell dimensions were derived: $a=13.211 \pm 0.006$, $b=8.617 \pm 0.003$, $c=13.962 \pm 0.005 \text{\AA}$, $\beta=116^\circ 51' \pm 2'$. The measured density has been reported (van Niekerk *et al.* 1953) as $1.79 \pm 0.02 \text{ g.cm}^{-3}$; from the derived cell dimensions and assuming four dinuclear molecules of formula weight $376.23 \text{ g.mole}^{-1}$, a density of 1.76 g.cm^{-3} was calculated. As in the case of the rhodium compound, systematic extinctions indicated that the space group should be Cc or $C2/c$.

The rhodium acetate crystal was aligned on the diffractometer with its $[\bar{1}12]$ axis coincident with the φ

axis of the goniometer. Data were collected for 1829 independent reflections (index sets hkl and $\bar{h}\bar{k}l$) within the sphere $\theta \leq 27.5^\circ$. The chromium acetate crystal was aligned so that its $[3\bar{1}\bar{1}]$ axis coincided with the φ axis, and the intensities of 1412 independent reflections within the sphere $\theta \leq 25.0^\circ$ (index sets hkl and $\bar{h}\bar{k}l$) were measured. On both data sets intensities were measured with a scintillation counter; the pulse-height discriminator was set to accept 95% of the $\text{Mo } K\alpha$ peak. The $\text{Mo } K\alpha$ radiation was filtered by zirconium foil. Distances from the crystal to the source and from the crystal to the circular screening aperture (2°) were 14.6 and 17.9 cm respectively. A moving-crystal moving-counter scan technique was employed with a scan range of 1.33° and a take-off angle of 2° . The scan rate was $4^\circ/\text{min}$.

Table 3. *Interatomic distances* (\AA) for $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2^1$

(a) Intramolecular bond distances		(b) Short intramolecular nonbonded distances	
Rh—Rh'	2.3855 (5)	Rh'—O(4)	3.084 (2)
Rh—O(5)	2.310 (3)	Rh'—O(1)	3.097 (2)
Rh'—O(3)	2.036 (3)	Rh'—C(3)	2.879 (3)
Rh—O(4)	2.029 (3)	Rh'—C(1)	2.895 (3)
Rh—O(1)	2.047 (3)	O(3)—O(2)	2.859 (3)
Rh'—O(2)	2.042 (4)	O(3)—O(1')	2.940 (3)
Average Rh—O	2.039 (8)	O(4')—O(2)	2.910 (3)
C(3)—O(3)	1.268 (5)	O(4)—O(1)	2.815 (3)
C(3)—O(4)	1.269 (6)	O(3)—O(4)	2.251 (4)
C(1)—O(1)	1.265 (5)	O(1)—O(2)	2.246 (4)
C(1)—O(2)	1.273 (3)	O(3)—C(4)	2.369 (4)
Average C—O	1.269 (4)	O(4)—C(4)	2.370 (6)
C(3)—C(4)	1.499 (5)	O(1)—C(2)	2.375 (5)
C(1)—C(2)	1.497 (6)	O(2)—C(2)	2.365 (4)
Average C—CH ₃	1.498 (2)	C(3)—H(41)	2.02 (7)
C(4)—H(41)	0.94 (9)	C(3)—H(42)	2.18 (7)
C(4)—H(42)	1.00 (6)	C(3)—H(43)	1.99 (7)
C(4)—H(43)	0.92 (9)	C(1)—H(22)	2.20 (5)
C(2)—H(22)	1.09 (8)	C(1)—H(23)	2.12 (7)
C(2)—H(23)	1.01 (7)	C(1)—H(21)	1.96 (9)
C(2)—H(21)	0.91 (7)		
(c) Short intermolecular distances		Vector between molecules	
O(5)—O(1)	2.943 (4)	$\frac{1}{2}-x$ $\frac{1}{2}-y$, z	
O(5)—O(2)	2.830 (4)	x , \bar{y} , $\frac{1}{2}+z$	
H(41)—H(41)	2.39 (9)	$-x$, y , $\frac{1}{2}-z$	
H(43)—H(21)	2.56 (9)	$\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$	

Integrated intensities (I) were obtained from the total counts (P) of a 20-sec coupled $2\theta-\omega$ scan from $2\theta_{\text{calc}}-0.66^\circ$ to $2\theta_{\text{calc}}+0.67^\circ$ and stationary background counts (B_1, B_2) of 10 sec duration at the limits of each scan. Assuming that the background varies linearly (or gives an equivalent integrated total) through the scan range, $I=P-B_1-B_2$. Five reflections on the rhodium acetate crystal that were checked at 4-hr intervals exhibited a maximum variation of $\pm 1\%$ which was random with time. Thus, there was no evidence of crystal decomposition. The five standard reflections for the chromium acetate crystal, checked at 4-hr intervals, exhibited a maximum variation of -3.5% which was nearly linear with time and independent of $\sin \theta/\lambda$. Intensities were corrected accordingly for an assumed decomposition.

All reflections except for those systematically absent were used in the solution and refinement of the structures (1573 reflections for the rhodium acetate, 1313 reflections for the chromous acetate). The metal atoms were located in three-dimensional Patterson maps. In the case of the chromium acetate, the oxygen atoms were also found. In both cases the conformity of the Patterson function with the requirements of space group $C2/c$ indicated that this, rather than Cc , was the correct one. The subsequent wellbehaved refinement of both structures to low discrepancy indices substantiates this choice. In the space group $C2/c$ it is required that the dinuclear formula units lie at crystallographic centers of inversion. Three-dimensional electron density difference syntheses, using structure factors with signs calculated from the atoms whose positions were found in the Patterson maps, gave coordinates for all remaining nonhydrogen atoms.

An absorption correction was made on the rhodium acetate data since $\mu=22.82 \text{ cm}^{-1}$ and a 13% variation in intensity of the (224) reflection was observed in a φ scan at $\chi=90^\circ$. Near the end of refinement of this structure a plot of $I_{\text{calc}}/I_{\text{obs}}$ versus I_{calc} gave evidence for significant secondary extinction, and intensities were corrected using $I_{\text{corr}}=I_{\text{obs}}(1+2gI_{\text{calc}})$ where $g=2.14 \times 10^{-7}$. Neither an absorption correction ($\mu=16.44$, estimated maximum transmission coefficient=0.720, estimated minimum transmission coefficient=0.67) nor an extinction correction was considered necessary for the chromium acetate data.

Both structures were refined by a full-matrix least-squares procedure, minimizing $\sum w(|F_o|-|F_c|)^2$. Scattering factors for nonhydrogen atoms (Cromer & Waber, 1965) and for hydrogen atoms (Mason & Robertson, 1966) were taken from the literature. Anomalous dispersion corrections (Cromer, 1965) were included in the calculated structure factors. Empirical weighting schemes that minimized the dependence of $w\Delta^2$ on the magnitude of F_o and on $(\sin \theta)/\lambda$ (Cruickshank, 1965) were as follows.

For rhodium acetate: $\sigma=w^{-\frac{1}{2}}=\sigma_o[-157.5(\sin \theta)/\lambda + 50.7]^\frac{1}{2}$ if $(\sin \theta)/\lambda < 0.25$; $\sigma=2.60\sigma_o$ of $(\sin \theta)/\lambda \geq 0.25$, where $\sigma_o=R \text{Lp}[P+B_1+B_2+(0.02I_o)^2]^\frac{1}{2}/2F_o$. Before switching to this weighting scheme, one based on counting statistics (*i.e.* $\sigma=\sigma_o$ for all F_o) was used; this led to a standard deviation for an observation of unit weight of 2.77. With the empirical scheme, this deviation immediately fell to 1.11.

For chromium acetate, weights based on counting statistics resulted in only a very slight and irregular dependence of $w\Delta^2$ on F_o . Minor adjustments to σ (small increases) for those regions of F_o so affected pro-

Table 4. Bond angles ($^\circ$) for $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$

Rh—Rh'—O(3)	87.95 (6)	H(41)—C(4)—H(42)	89 (5)
Rh'—Rh—O(4)	88.25 (5)	H(41)—C(4)—H(43)	124 (6)
Rh'—Rh—O(1)	88.31 (6)	H(42)—C(4)—H(43)	106 (7)
Rh—Rh'—O(2)	87.76 (6)	H(22)—C(2)—H(23)	116 (7)
Average Rh—Rh—O	88.07 (26)	H(22)—C(2)—H(21)	104 (7)
Rh'—O(3)—C(3)	119.36 (10)	H(23)—C(2)—H(21)	96 (7)
Rh—O(4)—C(3)	119.38 (13)	Average H—C—H	106 (13)
Rh—O(1)—C(1)	119.30 (11)	O(3)—Rh'—O(5')	90.23 (9)
Rh'—O(2)—C(1)	119.95 (15)	O(4)—Rh—O(5)	93.58 (10)
Average Rh—O—C	119.50 (30)	O(1)—Rh—O(5)	94.78 (9)
O(3)—C(3)—O(4)	125.0 (2)	O(2)—Rh'—O(5')	89.18 (11)
O(1)—C(1)—O(2)	124.6 (2)	O(3)—Rh'—O(2)	89.02 (7)
Average O—C—O	124.8 (3)	O(4)—Rh—O(1)	87.37 (10)
O(3)—C(3)—C(4)	117.5 (3)	Average O—Rh—O	90.7 (2.9)
O(4)—C(3)—C(4)	117.5 (2)	Rh—Rh'—O(5')	176.47 (6)
O(1)—C(1)—C(2)	118.4 (2)	O(3)—Rh'—O(4')	176.18 (9)
O(2)—C(1)—C(2)	117.0 (3)	O(1')—Rh'—O(2)	175.88 (10)
Average O—C—CH ₃	117.6 (6)		
C(3)—C(4)—H(41)	109 (3)		
C(3)—C(4)—H(42)	120 (4)		
C(3)—C(4)—H(43)	108 (3)		
C(1)—C(2)—H(22)	116 (2)		
C(1)—C(2)—H(23)	115 (4)		
C(1)—C(2)—H(21)	106 (4)		
Average C—C—H	112 (5)		

duced a good fit of all data to Cruickshank's criterion.

All nonhydrogen atoms were refined anisotropically using thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

For the rhodium acetate structure, at $R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|) = 0.049$, a difference Fourier map was computed and the methyl-hydrogen atoms were unambiguously located, but the water-hydrogen atoms could not be located either in this difference Fourier map or in the final one. The methyl-hydrogen atoms were refined isotropically while refinement of the other atoms was continued anisotropically. The refinement was considered complete when in one cycle no thermal or positional parameter changed by as much as $\frac{1}{5}$ its estimated standard deviation. After this final cycle of refinement R_1 was 0.027 and $R_2 = \{\sum w[|F_o| - |F_c|]^2 / \sum wF_o^2\}^{1/2} = 0.072$. However, $R_1 = 0.025$ and $R_2 = 0.031$ without the three reflections $\bar{1}18$, $\bar{3}78$ and $\bar{7}19$, which are suspected of being in error due to angular mis-setting since in all three cases F_{obs} is less than F_{calc} . In the final electron density difference map the standard deviation in the electron density (Cruickshank, 1949) was $0.11 \text{ e.}\text{\AA}^{-3}$. The highest peak in the difference map contained $0.42 \text{ e.}\text{\AA}^{-3}$. The estimated standard deviation of an observation of unit weight was 0.83.

In the chromium acetate structure at $R_1 = 0.054$ a difference Fourier map was computed, and the methyl- and water-hydrogen atoms were unambiguously located. The hydrogen atoms were refined isotropically

while the refinement of the other atoms was continued anisotropically. The refinement was considered complete when in one cycle no thermal or positional parameter changed by as much as $\frac{1}{10}$ of its e.s.d. for the heavy atoms and $\frac{1}{4}$ of its e.s.d. for the hydrogen atoms. After this final cycle of refinement, the values of R_1 and R_2 were 0.034 and 0.035 respectively. In the final electron density difference map, the standard deviation in the electron density was $0.06 \text{ e.}\text{\AA}^{-3}$. The highest peak in this map contained $0.33 \text{ e.}\text{\AA}^{-3}$. The standard deviation of an observation of unit weight was 0.74.

Table 5. *Molecular planes for* $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$

(a) Plane through Rh, O(3), C(3), O(4), Rh'
 $0.4993x + 0.0310y + 0.8659z = 0.0001$

Distance of atoms from plane (Å)

Rh'	0.0001	C(3)	0.0166
Rh	-0.0001	C(4)	0.0533
O(3)	-0.0157	O(5)	-0.12169
O(4)	-0.0009		

(b) Plane through Rh, O(2), C(1), O(1), Rh'
 $-0.4986x + 0.8405y + 0.2120z = 0.0002$

Distance of atoms from plane (Å)

Rh'	0.0002	C(1)	0.0196
Rh	-0.0002	C(2)	0.0971
O(1)	0.0125	O(5)	-0.0698
O(2)	-0.0321		

Dihedral angle = $92^\circ 15'$

Table 6. *Atomic coordinates for* $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$

	x	y	z	$B(\text{\AA}^2)$
Cr	0.04466 (3)	0.07428 (5)	-0.04118 (3)	
O(1)	0.1846 (1)	0.0872 (2)	0.1030 (1)	
O(2)	0.1020 (1)	-0.0575 (2)	0.1795 (1)	
O(3)	-0.0967 (1)	0.1272 (2)	0.0766 (1)	
O(4)	-0.0111 (2)	0.2666 (2)	0.0001 (1)	
O(5)	0.1269 (2)	0.2027 (3)	-0.1301 (2)	
C(1)	0.1847 (2)	0.0226 (3)	0.1843 (2)	
C(2)	0.2847 (3)	0.0415 (5)	0.2910 (3)	
C(3)	-0.0683 (2)	0.2555 (3)	0.0517 (2)	
C(4)	-0.1040 (3)	0.4015 (4)	0.0853 (3)	
H(21)	0.261 (3)	0.071 (5)	0.339 (3)	6.2 (1.0)
H(22)	0.335 (3)	0.092 (4)	0.290 (3)	4.8 (0.8)
H(23)	0.317 (4)	-0.056 (6)	0.326 (4)	8.4 (1.3)
H(41)	-0.096 (3)	0.391 (5)	0.152 (4)	5.9 (0.9)
H(42)	-0.074 (4)	0.484 (5)	0.073 (3)	6.6 (1.0)
H(43)	-0.175 (4)	0.399 (5)	0.053 (3)	6.7 (1.0)
H(51)	0.120 (3)	0.162 (4)	-0.183 (3)	4.4 (0.8)
H(52)	0.171 (3)	0.257 (4)	-0.113 (3)	4.8 (0.9)

Table 7. *Thermal parameters* (\AA^2) *for* $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	1.549 (18)	1.776 (18)	1.526 (17)	-0.049 (13)	0.696 (13)	-0.053 (13)
O(1)	1.83 (7)	2.69 (8)	1.88 (7)	-0.22 (6)	0.76 (6)	0.04 (6)
O(2)	1.99 (7)	2.94 (9)	1.77 (7)	-0.28 (7)	0.62 (6)	0.17 (6)
O(3)	2.59 (8)	2.29 (8)	2.83 (8)	0.08 (7)	1.64 (7)	-0.22 (7)
O(4)	2.80 (8)	2.00 (7)	2.91 (7)	0.26 (9)	1.55 (7)	-0.13 (6)
O(5)	4.21 (11)	3.47 (11)	2.97 (10)	-1.69 (10)	2.46 (9)	-1.05 (9)
C(1)	1.81 (10)	2.26 (11)	1.94 (10)	0.10 (9)	0.76 (9)	-0.20 (9)
C(2)	2.54 (14)	5.71 (21)	2.16 (13)	-1.39 (14)	0.22 (11)	0.20 (14)
C(3)	1.67 (10)	2.36 (12)	1.93 (11)	0.30 (9)	0.40 (9)	-0.38 (9)
C(4)	3.22 (16)	2.76 (15)	3.99 (17)	0.34 (13)	1.78 (14)	-0.74 (13)

Table 8. *Interatomic distances (Å) for*
 $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$

(a) Intramolecular bond distances		(b) Short intramolecular nonbonded distances	
Cr—Cr'	2.362 (1)	Cr—O(2)	3.041 (2)
Cr—O(5)	2.272 (3)	Cr—O(3)	3.029 (2)
Cr—O(1)	2.030 (2)	Cr—C(1)	2.876 (3)
Cr'—O(2)	2.031 (2)	Cr—C(3)	2.845 (3)
Cr'—O(3)	2.009 (2)	O(1)—O(4)	2.789 (3)
Cr—O(4)	2.001 (2)	O(1)—O(3)	2.902 (3)
Average Cr—O	2.018 (8)	O(2')—O(4)	2.873 (3)
		O(2)—O(3)	2.843 (3)
		O(1)—O(2)	2.222 (3)
C(1)—O(1)	1.263 (4)	O(3)—O(4)	2.226 (3)
C(1)—O(2)	1.268 (4)	O(1)—C(2)	2.378 (4)
C(3)—O(3)	1.266 (3)	O(2)—C(2)	2.363 (4)
C(3)—O(4)	1.262 (4)	O(3)—C(4)	2.372 (4)
Average C—O	1.265 (5)	O(4)—C(4)	2.366 (5)
		C(1)—H(4)	1.97 (4)
C(1)—C(2)	1.488 (4)	C(1)—H(22)	1.96 (3)
C(3)—C(4)	1.492 (5)	C(1)—H(23)	2.08 (4)
Average C—CH ₃	1.490 (5)	C(3)—H(41)	1.98 (5)
		C(3)—H(42)	2.00 (5)
C(2)—H(21)	0.89 (6)	C(3)—H(43)	1.88 (5)
C(2)—H(22)	0.80 (4)	Cr—H(51)	2.69
C(2)—H(23)	0.97 (5)	Cr—H(52)	2.78
C(4)—H(41)	0.89 (5)		
C(4)—H(42)	0.87 (5)		
C(4)—H(43)	0.84 (5)		
Average C—H	0.88 (8)		
O(5)—H(51)	0.79 (4)		
O(5)—H(52)	0.70 (4)		
Average O(5)—H	0.74 (5)		

(c) Intermolecular distances

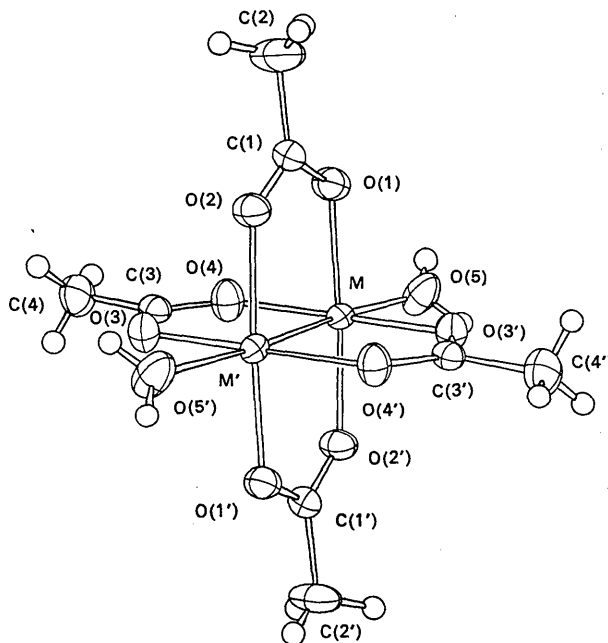
	Vector between molecules		
O(5)—O(1)	2.962	$\frac{1}{2}$, $\frac{1}{2}$, 0	
O(5)—O(2)	2.820	0 0 $-\frac{1}{2}$	

Table 9. *Bond angles (°) for* $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$

Cr—Cr'—O(3)	87.32 (4)	H(21)—C(2)—H(22)	116 (5)
Cr'—Cr—O(4)	88.80 (5)	H(21)—C(2)—H(23)	95 (3)
Cr'—Cr—O(1)	88.76 (5)	H(22)—C(2)—H(23)	108 (4)
Cr—Cr'—O(2)	87.27 (5)	H(41)—C(4)—H(42)	117 (5)
Average Cr—Cr—O	88.04 (30)	H(41)—C(4)—H(43)	97 (5)
		H(42)—C(4)—H(43)	115 (5)
Cr'—O(2)—C(1)	121.21 (17)	Average H—C—H	108 (8)
Cr'—O(3)—C(3)	120.71 (15)	O(1)—Cr—O(5)	93.97 (9)
Cr—O(4)—C(3)	119.67 (12)	O(2')—Cr—O(5)	90.08 (9)
Cr—O(1)—C(1)	119.85 (9)	O(3')—Cr—O(5)	89.15 (8)
Average Cr—O—C	120.36 (45)	O(4)—Cr—O(5)	94.75 (8)
		Average O—Cr—O(5)	92.0 (10)
O(1)—C(1)—O(2)	122.7 (1)	O(1)—Cr—O(4)	87.57 (6)
O(3)—C(3)—O(4)	123.4 (2)	O(1)—Cr—O(3')	91.84 (8)
Average O—C—O	123.1 (3)	O(4)—Cr—O(2')	90.88 (8)
		O(2')—Cr—O(3')	89.44 (6)
O(1)—C(1)—C(2)	119.4 (2)	Average O—Cr—O	89.9 (8)
O(2)—C(1)—C(2)	117.8 (2)	Cr'—Cr—O(5)	175.61 (11)
O(3)—C(3)—C(4)	118.4 (2)	O(1)—Cr—O(2')	175.76 (10)
O(4)—C(3)—C(4)	118.2 (2)	O(4)—Cr—O(3')	176.08 (10)
Average O—C—CH ₃	118.5 (5)		
C(1)—C(2)—H(21)	109 (2)		
C(1)—C(2)—H(22)	114 (2)		
C(1)—C(2)—H(23)	114 (2)		
C(3)—C(4)—H(41)	110 (2)		
C(3)—C(4)—H(42)	112 (2)		
C(3)—C(4)—H(43)	104 (3)		
Average C—C—H	111 (5)		

Results

The molecular structure of the chromium compound is shown in Fig. 1; the two molecules are isostructural in the true sense of the word so that, aside from slight quantitative discrepancies, this may be considered to

Fig. 1. A convenient projection of the molecular structure of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ and $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$. The numbering scheme used in all tables is shown.

represent the rhodium structure as well. The atom numbering scheme shown in Fig. 1 applies to both molecules for which structure parameters are given in Tables 1 through 10.

Table 10. *Molecular planes for Cr₂(O₂CCH₃)₄(H₂O)₂*

(a) Plane through Cr, O(1), O(2), O(5), C(1), C(2)
-0.4858x + 0.8475y + 0.2138z = 0.0147

Distance of atoms from plane (Å)			
Cr	0.0053	O(5)	-0.0939
O(1)	0.0278	C(1)	0.0202
O(2)	-0.0617	C(2)	0.1272

(b) Plane through Cr, O(3), O(4), O(5), C(3), C(4)
0.5088x + 0.0468y + 0.8596z = 0.017968

Distance of atoms from plane (Å)			
Cr	0.0035	O(5)	-0.0589
O(3)	-0.0421	C(3)	0.0139
O(4)	0.0158	C(4)	0.0845



Atomic positional parameters and thermal parameters are given in Tables 1 and 2. Interatomic distances

and bond angles are listed in Tables 3 and 4. Table 5 shows the equations for several best-mean planes defined relative to an orthogonal coordinate system in which X is collinear with a and Y is collinear with b.



Atomic positional parameters, thermal vibration parameters, interatomic distances and bond angles for this compound are reported in Tables 6 through 9, respectively. Parameters of least-squares planes, referred to the same orthogonal coordinate system mentioned for the rhodium compound, are given in Table 10.

The calculated and observed structure factors are given in Tables 11 and 12 for the rhodium and chromium compounds respectively. Standard deviations in all distances (Tables 3 & 8) include all correlations with correlation coefficients greater than 0.20.

Fig. 2 shows a projection of both structures on the (010) plane. Hydrogen-bonded contacts as observed in the chromium compound are indicated by dotted lines.

Table 11. *Observed and calculated structure factors of chromium acetate (× 10)*

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	0	0	100	100	0	0	0	100	100	0	0	0	100	100	0	0	0	100	100
0	0	1	125	125	0	0	1	125	125	0	0	2	250	250	0	0	3	375	375
0	0	2	500	500	0	0	3	625	625	0	0	4	1000	1000	0	0	5	1375	1375
0	1	0	150	150	0	1	0	150	150	0	1	1	150	150	0	1	2	300	300
0	1	1	200	200	0	1	1	200	200	0	1	2	250	250	0	1	3	300	300
0	1	2	250	250	0	1	3	300	300	0	1	4	350	350	0	1	5	400	400
0	2	0	200	200	0	2	0	200	200	0	2	0	200	200	0	2	2	400	400
0	2	1	250	250	0	2	1	250	250	0	2	2	250	250	0	2	3	300	300
0	2	2	300	300	0	2	3	300	300	0	2	4	350	350	0	2	5	400	400
1	0	0	100	100	1	0	0	100	100	1	0	0	100	100	1	0	0	100	100
1	0	1	150	150	1	0	1	150	150	1	0	1	150	150	1	0	2	300	300
1	0	2	200	200	1	0	2	200	200	1	0	2	200	200	1	0	3	300	300
1	0	3	250	250	1	0	3	250	250	1	0	4	300	300	1	0	5	350	350
1	1	0	150	150	1	1	0	150	150	1	1	0	150	150	1	1	1	300	300
1	1	1	200	200	1	1	1	200	200	1	1	2	250	250	1	1	3	300	300
1	1	2	250	250	1	1	3	300	300	1	1	4	350	350	1	1	5	400	400
1	2	0	200	200	1	2	0	200	200	1	2	0	200	200	1	2	2	400	400
1	2	1	250	250	1	2	1	250	250	1	2	2	250	250	1	2	3	300	300
1	2	2	300	300	1	2	3	300	300	1	2	4	350	350	1	2	5	400	400
2	0	0	100	100	2	0	0	100	100	2	0	0	100	100	2	0	0	100	100
2	0	1	150	150	2	0	1	150	150	2	0	1	150	150	2	0	2	300	300
2	0	2	200	200	2	0	2	200	200	2	0	2	200	200	2	0	3	300	300
2	0	3	250	250	2	0	3	250	250	2	0	4	300	300	2	0	5	350	350
2	1	0	150	150	2	1	0	150	150	2	1	0	150	150	2	1	1	300	300
2	1	1	200	200	2	1	1	200	200	2	1	2	250	250	2	1	3	300	300
2	1	2	250	250	2	1	3	300	300	2	1	4	350	350	2	1	5	400	400
2	2	0	200	200	2	2	0	200	200	2	2	0	200	200	2	2	2	400	400
2	2	1	250	250	2	2	1	250	250	2	2	2	250	250	2	2	3	300	300
2	2	2	300	300	2	2	3	300	300	2	2	4	350	350	2	2	5	400	400
3	0	0	100	100	3	0	0	100	100	3	0	0	100	100	3	0	0	100	100
3	0	1	150	150	3	0	1	150	150	3	0	1	150	150	3	0	2	300	300
3	0	2	200	200	3	0	2	200	200	3	0	2	200	200	3	0	3	300	300
3	0	3	250	250	3	0	3	250	250	3	0	4	300	300	3	0	5	350	350
3	1	0	150	150	3	1	0	150	150	3	1	0	150	150	3	1	1	300	300
3	1	1	200	200	3	1	1	200	200	3	1	2	250	250	3	1	3	300	300
3	1	2	250	250	3	1	3	300	300	3	1	4	350	350	3	1	5	400	400
3	2	0	200	200	3	2	0	200	200	3	2	0	200	200	3	2	2	400	400
3	2	1	250	250	3	2	1	250	250	3	2	2	250	250	3	2	3	300	300
3	2	2	300	300	3	2	3	300	300	3	2	4	350	350	3	2	5	400	400

Discussion

The most significant fact about these accurately determined structures, as reported here, is that in the values of certain critical molecular dimensions they differ greatly from those reported previously. The differences are so large to require reconsideration of all conclusions concerning the bonding and electronic structures which were based on the older structural parameters. Briefly, in place of previously postulated weak metal-metal interactions in both the chromium (Figgis & Martin, 1956; Cotton, 1967) and rhodium (Dubicki & Martin, 1970) compounds, it now appears that strong bonds, quadruple in the chromium case and triple in the rhodium case, must exist between the metal atoms

(Cotton, Deboer, LaPrade, Pipal & Ucko, 1970; Caulton & Cotton, 1971). The consequences of the structural parameters in terms of bonding will be discussed more fully elsewhere; this report is primarily concerned with reporting the structures themselves in detail.

All C-C and C-O distances in both molecules are normal. The acetate-oxygen to water-oxygen contacts between neighboring molecules (2.83 and 2.94 Å in the rhodium compound and 2.82 and 2.96 Å in the chromium compound) suggest the presence of weak to moderately strong hydrogen bonds. In the case of the chromium compound the locations of the water-hydrogen atoms near the interuclear axes confirm this.

Features of greatest interest in each case are the overall molecular configurations, the metal-to-metal

Table 12. Observed and calculated structure factors of rhodium acetate ($\times 10$)

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	0	0	8000	7998	1	1	0	800	798	2	0	0	800	798	3	0	0	800	798
1	0	0	800	798	4	0	0	800	798	5	0	0	800	798	6	0	0	800	798
2	0	0	800	798	7	0	0	800	798	8	0	0	800	798	9	0	0	800	798
3	0	0	800	798	10	0	0	800	798	11	0	0	800	798	12	0	0	800	798
4	0	0	800	798	13	0	0	800	798	14	0	0	800	798	15	0	0	800	798
5	0	0	800	798	16	0	0	800	798	17	0	0	800	798	18	0	0	800	798
6	0	0	800	798	19	0	0	800	798	20	0	0	800	798	21	0	0	800	798
7	0	0	800	798	22	0	0	800	798	23	0	0	800	798	24	0	0	800	798
8	0	0	800	798	25	0	0	800	798	26	0	0	800	798	27	0	0	800	798
9	0	0	800	798	28	0	0	800	798	29	0	0	800	798	30	0	0	800	798
10	0	0	800	798	31	0	0	800	798	32	0	0	800	798	33	0	0	800	798
11	0	0	800	798	34	0	0	800	798	35	0	0	800	798	36	0	0	800	798
12	0	0	800	798	37	0	0	800	798	38	0	0	800	798	39	0	0	800	798
13	0	0	800	798	40	0	0	800	798	41	0	0	800	798	42	0	0	800	798
14	0	0	800	798	43	0	0	800	798	44	0	0	800	798	45	0	0	800	798
15	0	0	800	798	46	0	0	800	798	47	0	0	800	798	48	0	0	800	798
16	0	0	800	798	49	0	0	800	798	50	0	0	800	798	51	0	0	800	798
17	0	0	800	798	52	0	0	800	798	53	0	0	800	798	54	0	0	800	798
18	0	0	800	798	55	0	0	800	798	56	0	0	800	798	57	0	0	800	798
19	0	0	800	798	58	0	0	800	798	59	0	0	800	798	60	0	0	800	798
20	0	0	800	798	61	0	0	800	798	62	0	0	800	798	63	0	0	800	798
21	0	0	800	798	64	0	0	800	798	65	0	0	800	798	66	0	0	800	798
22	0	0	800	798	67	0	0	800	798	68	0	0	800	798	69	0	0	800	798
23	0	0	800	798	70	0	0	800	798	71	0	0	800	798	72	0	0	800	798
24	0	0	800	798	73	0	0	800	798	74	0	0	800	798	75	0	0	800	798
25	0	0	800	798	76	0	0	800	798	77	0	0	800	798	78	0	0	800	798
26	0	0	800	798	79	0	0	800	798	80	0	0	800	798	81	0	0	800	798
27	0	0	800	798	82	0	0	800	798	83	0	0	800	798	84	0	0	800	798
28	0	0	800	798	85	0	0	800	798	86	0	0	800	798	87	0	0	800	798
29	0	0	800	798	88	0	0	800	798	89	0	0	800	798	90	0	0	800	798
30	0	0	800	798	91	0	0	800	798	92	0	0	800	798	93	0	0	800	798
31	0	0	800	798	94	0	0	800	798	95	0	0	800	798	96	0	0	800	798
32	0	0	800	798	97	0	0	800	798	98	0	0	800	798	99	0	0	800	798
33	0	0	800	798	100	0	0	800	798	101	0	0	800	798	102	0	0	800	798

distances and the metal-to-ligand distances. The present work fully confirms the previous reports that the molecules have what is often called the 'copper acetate structure' with four bridging carboxylate groups lying in two mutually perpendicular planes. The molecules have crystallographically rigorous $\bar{1}$ symmetry and, neglecting hydrogen atoms, $4/mmm$ virtual symmetry. In each case the metal-to-metal distances are short, the metal-to-acetate oxygen distances seem normal and the metal-to-OH₂ distances are long.

If the metal-to-acetate oxygen distances are considered appropriate to normal single bonds, and the usual covalent single-bond radius of oxygen (0.66 Å) is subtracted from the mean of the Cr-O(ac) and Rh-O(ac) distances in each case, metal single-bond radii of 1.36 Å (Cr) and 1.38 Å (Rh) are obtained. When these figures are doubled, distances of 2.72 and 2.76 Å are obtained as compared to the observed M-M distances of 2.36 and 2.39 Å, respectively. Thus, in both cases the M-M bonds appear to be substantially shorter than single bonds would be expected to be. In the metals the distances are 2.50 Å (Cr) and 2.69 Å (Rh). The M-OH₂ distances are both considerably longer than the M-O(ac) distances, by 0.25 and 0.27 Å for the chromium and rhodium compounds, respectively, thus showing that the water molecules are only weakly coordinated.

Since the hydrogen atoms were found in the chromium acetate structure, it is possible to consider the detailed mode of interaction between the water molecule and chromium atom. The extreme possibilities are:

(a) An essentially tetrahedral disposition of two O-H bonding pairs and two lone pairs of oxygen electrons with one lone pair being donated to a σ orbital of the metal. In this case the angle between the twofold axis of the water molecule and the fourfold axis of the skeleton of the entire molecule should be 54.8°.

(b) An essentially trigonal set of σ orbitals on oxygen, two bonding to H and one to the metal, with the

remaining electron pair occupying an oxygen p orbital. In this case, the twofold axis of H₂O and the molecular fourfold axis should be colinear. In fact, the angle in question has the value $15 \pm 5^\circ$ if referred to the Cr-Cr' axis and $19 \pm 5^\circ$ if referred to the Cr-O line.

Thus, while it comes closer to case (b) than to case (a), it is sufficiently far from either limiting case to suggest an intermediate type of interaction.

The following programs for the IBM 360/65 computer were used and are gratefully acknowledged: (1) *PICK2* (J. A. Ibers) to calculate diffractometer settings and least-squares unit-cell dimensions, (2) *FOR-DAP* (A. Zalkin) Fourier synthesis program, (3) *SFLS5* (C. T. Prewitt) full-matrix least-squares refinement program, (4) *GONO9* (W. C. Hamilton) for the absorption correction, (5) *DISTAN* (D. P. Shoemaker) to calculate intermolecular contacts, (6) *MGEOM* (J. S. Wood) to calculate least-squares planes, (7) *ORTEP* (C. Johnson) to calculate and plot molecular structures including thermal ellipsoids, (8) *PUBTAB* (R. C. Elder) to prepare compact tabulation of structure factors.

Data reduction, distance, angle and e.s.d.'s on distances and angles were calculated using programs written by the authors.

We are grateful to the U.S. Atomic Energy Commission for partial support of this work. J.R.P. acknowledges an NDEA fellowship during the period 1968-70.

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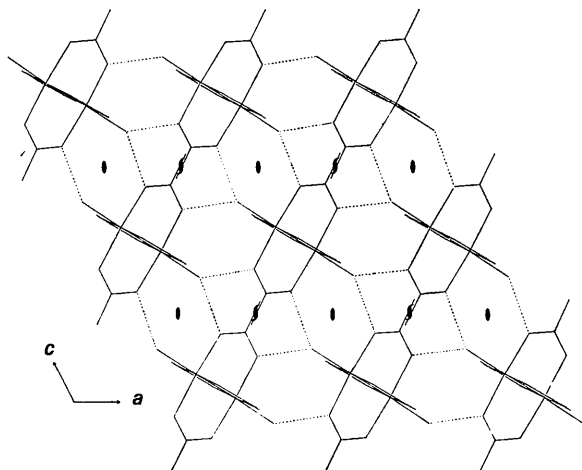


Fig. 2. Projection of 9 molecular units on [010]. Dashed lines represent hydrogen bonding.