ion has a distorted octahedral coordination geometry involving Cl, O(1), O(3), O(6), O(8), and O(10) with distances of 2.744 (7), 2.495 (9), 2.75 (1), 2.52 (1), 2.35 (1), and 2.44 (1) Å, respectively.

Discussion

An examination of the bond distances and angles in Tables IV and V for compounds **1** and **2** reveals that the $Rh_2(CO_3)_4^{4-}$ units are essentially identical. The only structural parameter which differs significantly between the two compounds is the Rh–axial ligand distance, as might be expected. The Rh–O(7) distance in **1** of 2.344 (5) Å is to be compared with a value of 2.310 (3) Å found in $Rh_2(OAc)_4(H_2O)_2$.[8] The slightly weaker (0.034 Å) Rh–O axial bond in the carbonate complex is matched with a slightly stronger Rh–Rh bond (by ~0.008 Å), and once again, the persistent inverse relationship between metal–metal and metal–axial ligand bond lengths[13-15] is observed. In complex **2** the axial position is occupied by a Cl^- ion which is associated with the Rh atom at a distance of 2.601 (3) Å. Such a long distance precludes any but the weakest type of bonding interaction. The high negative charge already on the complex undoubtedly contributes to a lengthening of the Rh–Cl bond. In contrast, the Rh–Cl bond length in $[C(NH_2)_3][Rh_2(OAc)_4Cl_2]$, where $[C(NH_2)_3]^+$ is the guanidinium ion, is significantly shorter with a value of 2.49 Å,[16] but here there is no negative charge on the $Rh_2(OAc)_4$ unit tending to repel the incoming Cl^- ion as in the carbonate complex **2**.

A recent survey[2] of some 48 metal tetracarboxylate structures including 6 rhodium(II) acetate adducts reveals that the M–O–C and O–C–O angles are the most responsive to changes in M–M bond length. The average Rh–O–C and O–C–O angles in the two carbonate complexes are nearly identical with values of 120.3 (4) and 122.6 (6)° for **1** and 120.3 (4)° and 122.5 (1.0)° for **2**. The Rh–O–C angles are slightly greater than in $Rh_2(OAc)_4(H_2O)_2$[8] for which the angle is 119.5 (3)°, while the O–C–O angles in the carbonates are slightly less than the angle in the acetate complex (124.8 (3)°). Both of these angular variations are in accord with the shorter Rh–Rh distances observed in the two carbonate structures presented here.

The $[Rh_2(CO_3)_4]^{4-}$ ion is one of only two such carbonate-bridged dimetal units to be prepared, the other being the $[Cr_2(CO_3)_4]^{4-}$ ion.[6] Since the bridging carbonate ion appears to be completely compatible with the retention of the usual metal–metal bond lengths in these two cases, it seems likely that carbonato-bridged species should be stable for other dimetal ions such as Mo_2^{4+} and Re_2^{6+}, but it appears that no effort has been made yet to isolate them.

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Registry No. **1**, 72207-19-3; **2**, 72207-20-6; $Rh_2(O_2CCH_3)_4$, 15956-28-2; $Na_4[Rh_2(CO_3)_4]$, 53078-66-3.

Supplementary Material Available: Tables of observed and calculated structure factors for the two compounds (14 pages). Ordering information is given on any current masthead page.

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Structural Studies of Three Tetrakis(carboxylato)dirhodium(II) Adducts in Which Carboxylate Groups and Axial Ligands Are Varied

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Three dirhodium(II) compounds, namely, $Rh_2(O_2CCMe_3)_4(H_2O)_2$ (**1**), $Rh_2(O_2CCH_3)_4(THT)_2$ (**2**), and $Rh_2(O_2CCH_3)_4(Me_2SO)_2$ (**3**) (THT = tetrahydrothiophene, Me_2SO = dimethyl sulfoxide), have been prepared and their structures determined by X-ray crystallography. These structures were refined to final R_1 values of 0.036, 0.032, and 0.036 for **1**, **2**, and **3**, respectively. Compound **1** crystallizes in the space group $P\bar{1}$ with a = 9.408 (1) Å, b = 11.799 (2) Å, c = 6.984 (1) Å, α = 105.98 (1)°, β = 94.24 (1)°, γ = 99.48 (1)°, and Z = 1. The centrosymmetric structure has a relatively short Rh–Rh bond length of 2.371 (1) Å with axially coordinated water molecules at a distance of 2.295 (2) Å. Compound **2** crystallizes in the space group *Pbcn* with four formula weights in a unit cell having the dimensions a = 9.801 (2) Å, b = 16.087 (3) Å, and c = 14.592 (3) Å. The complex is located on a crystallographic center of inversion with a Rh–Rh bond length of 2.413 (1) Å and an axial Rh–S(THT) distance of 2.517 (1) Å. Crystals of **3** are orthorhombic, space group *Pbca*, with four formula units located on inversion centers in a unit cell having the dimensions a = 8.377 (2) Å, b = 16.726 (2) Å, and c = 14.840 (2) Å. The Me_2SO molecules coordinate through the sulfur atoms with a Rh–S distance of 2.451 (1) Å. The Rh–Rh bond length in **3** of 2.406 (1) Å is very slightly shorter than the value found for the THT adduct.

Introduction

Transition-metal tetracarboxylates of the form $M_2(O_2CR)_4L_2$ have played a key role in unraveling the effects of bridging ligands, as controlled by the R group substituents, and axial donor ligands on the metal–metal bond length. Structural studies of dichromium(II) tetracarboxylates reveal that a wide (~0.3 Å) range of Cr–Cr distances is possible from 2.214 (1) Å[1] (R = O^-, L = H_2O) to 2.541 (1) Å[2] (R = CF_3, L = OEt_2). A considerably narrower range of metal–metal bond lengths has been found for the second-row transition metals. The dimolybdenum(II) tetracarboxylates, for example, display only about a 0.04 Å variation in Mo–Mo bond length from 2.088 (1) Å in $Mo_2(piv)_4$[3] (piv = O_2CCMe_3 and L is an oxygen atom from a bridging pivalate group of a neighboring molecule) to 2.129 (2) Å in $Mo_2(O_2CCF_3)_4(py)_2$.[4] Generally

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shorter metal–metal distances have been observed with strongly electron-donating R group substituents like O^- or $C(CH_3)_3$ and weakly σ-donating axial ligands such as H_2O, although there have been apparent anomalies.[5,6]

The dirhodium(II) tetracarboxylates have afforded a wider variation in axial ligands than either the dichromium(II) or dimolybdenum(II) complexes because of the greater stability of the +2 oxidation state of rhodium toward oxidation and the relative inertness of the carboxylate ligands toward substitution. Structural studies of rhodium(II) acetate adducts in this laboratory and by Christoph and Koh[8-10] have established a range of Rh–Rh bond distances from 2.3855 (5) Å in $Rh_2(OAc)_4(H_2O)_2$[7] to 2.4555 (5) Å in $Rh_2(OAc)_4(P(OMe)_3)_2$.[9] In addition to those adducts in which these are ligands that span nearly the full range of weak and strong σ-donor ability, others have been prepared and structurally characterized with ligands that range from those with little or no π-accepting ability ($NHEt_2$[10]) to those which are strong π acceptors (CO, PF_3[9]).

The present work extends the dirhodium(II) tetracarboxylate series with the first pivalate complex of rhodium(II) in order to provide information on R group substituent effects and two additional adducts of rhodium(II) acetate with sulfur-donor ligands: tetrahydrothiophene (THT) and dimethyl sulfoxide (Me_2SO). The Me_2SO ligand is ambidentate and the structural results presented here on the Rh–S linkage isomer point to the "soft acid" character of the rhodium(II) tetraacetate nucleus.

Experimental Section

Compound Preparation. Rhodium(II) acetate was prepared by a literature method.[11]

$Rh_2(piv)_4(H_2O)_2$ (**1**) was prepared by heating $Rh_2(OAc)_4$ (0.1 g) in pivalic acid (2 mL) at 130 °C under Ar for 30 min. After cooling of the mixture to room temperature, dark blue-green crystals were deposited. The excess pivalic acid was removed by placing the mixture in a vacuum desiccator over P_2O_5 for several days. Further drying in an oven at 140 °C left a light green powder which was dissolved in a 1:1 mixture of $CHCl_3$–benzene. The solution was evaporated slowly with exposure to the laboratory atmosphere to yield dark green crystals of $Rh_2(piv)_4(H_2O)_2$ (**1**).

$Rh_2(OAc)_4(THT)_2$ (**2**) was prepared by suspending $Rh_2(OAc)_4$ in benzene (10 mL) and adding THT (10 mL). The resulting deep red solution was slowly evaporated yielding beautiful, large, dark red crystals of up to 3 mm in length.

$Rh_2(OAc)_4(Me_2SO)_2$ (**3**) was isolated by slow evaporation of an aqueous solution (5 mL) of $Rh_2(OAc)_4$ to which 5 mL of Me_2SO was added. The compound crystallized as orange prisms.

X-ray Crystallography. Collection of Data. Diffraction data for compounds **1** and **3** were collected at 26 ± 1 °C on an Enraf-Nonius CAD-4F autodiffractometer using Mo K$\bar{\alpha}$ radiation (λ = 0.71073 Å) with a graphite crystal monochromator in the incident beam. The final unit cell parameters for **1** were determined from a least-squares fit of 25 reflections in the range 28° < 2θ < 32° and are presented in Table I along with other pertinent crystallographic data. The final lattice constants for compound **3** were determined from a least-squares fit to 18 reflections in the range 26° < 2θ < 32° and these and other data are also given in Table I. Additional details concerning the data collection technique have appeared elsewhere.[12] The data for both **1** and **3** were corrected for Lorentz and polarization effects but not absorption.

Table I. Crystallographic Data for the Three Compounds

parameter	1	2	3
space group	$P\bar{1}$	*Pbcn*	*Pbca*
a, Å	9.408 (1)	9.801 (2)	8.377 (2)
b, Å	11.799 (2)	16.087 (3)	16.726 (2)
c, Å	6.984 (1)	14.592 (3)	14.840 (2)
α, deg	105.98 (1)	90.0	90.0
β, deg	94.24 (1)	90.0	90.0
γ, deg	99.48 (1)	90.0	90.0
V, Å^3	729.3 (4)	2300.6 (7)	2079 (1)
d_{calcd}, g/cm^3	1.47	1.78	1.91
Z	1	4	4
fw	646.35	618.33	598.26
cryst size, mm	0.2 × 0.2 × 0.5	0.2 × 0.3 × 0.3	0.2 × 0.2 × 0.5
μ(Mo Kα), cm^{-1}	11.442	16.053	17.796
range 2θ, deg	3–50	3–50	3–50
no. unique data	2564	1677	1815
no. data, $F_o^2 > 3\sigma(F_o^2)$	2360	1576	1442
no. variables	145	127	118
R_1	0.036	0.032	0.036
R_2	0.060	0.050	0.059
esd	1.893	1.199	1.702
largest peak,[a] e/Å^3	0.46	0.33	0.38

[a] Largest peak in the final difference Fourier map.

X-ray data for compound **2** were collected at 22 ± 3 °C on a Syntex $P\bar{1}$ autodiffractometer using Mo K$\bar{\alpha}$ radiation (λ = 0.71073 Å) with a graphite crystal monochromator. Crystallographic data are summarized in Table I. The lattice constants were determined from a least-squares fit to the setting angles of 15 reflections in the range 28° < 2θ < 32°. Further details concerning data collection on the Syntex $P\bar{1}$ autodiffractometer have appeared elsewhere.[13] Lorentz and polarization corrections were applied to the data but no absorption correction was made.

Solution and Refinement of the Structures.[14] The position of the Rh atom in $Rh_2(piv)_4(H_2O)_2$ (**1**) was obtained from the highest peak in the Patterson map. The refinement was begun in the space group $P\bar{1}$ and several least-squares cycles followed by difference Fourier maps rapidly led to the location of all 16 atoms in the structure. Anisotropic thermal parameters were assigned to all 16 atoms and subsequent least-squares refinement gave the final discrepancy indices shown in Table I defined by $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. The final difference Fourier map was featureless. No attempt was made to locate the hydrogen atoms.

Diffraction data for $Rh_2(OAc)_4(THT)_2$ (**2**) were collected for an orthorhombic crystal system. Subsequent examination of the data revealed systematic absences consistent with the space group *Pbcn*: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h + k = 2n + 1$. Since the cell volume was appropriate for only four formula units, the structure was required to be located on a twofold axis or an inversion center. From a three-dimensional Patterson function the position of the Rh atom was obtained and was found to be situated about an inversion center at (0, 0, 0). Refinement of the Rh atom position followed by a difference Fourier map revealed the positions of the remaining 13 atoms. Further least-squares refinement with anisotropic thermal parameters for all 14 atoms led to final discrepancy factors listed in

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(5) One example is $Cr_2(piv)_4$[3] with a Cr–Cr distance of 2.388 (4) Å, which is substantially longer than the 2.288 (2) Å distance in $Cr_2(OAc)_4$.[6] A consideration of differences in molecular packing for these two compounds including variations in weak axial interactions (Cr–O′ distances for $Cr_2(piv)_4$ average 2.45 Å, while they are only 2.327 Å in $Cr_2(OAc)_4$, where O′ denotes an oxygen atom from a neighboring bridging carboxylate ligand) does not in any straightforward way explain the Cr–Cr bond length variations.

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(14) All crystallographic computing was done on a PDP 11/45 computer at the Molecular Structure Corp., College Station, TX, with the Enraf-Nonius structure determination package with local modifications.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(piv)_4(H_2O)_2$ (1)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	0.43898 (2)	0.48302 (2)	0.63503 (3)	2.91 (1)	3.26 (1)	1.95 (1)	0.63 (1)	0.03 (1)	0.950 (9)
O(1)	0.6665 (3)	0.6773 (2)	0.5566 (4)	4.0 (1)	3.65 (9)	3.8 (1)	−0.10 (9)	−0.13 (9)	1.17 (8)
O(2)	0.7140 (3)	0.4288 (2)	0.4435 (4)	3.66 (9)	4.56 (9)	3.60 (9)	1.60 (8)	0.67 (8)	1.60 (8)
O(3)	0.5547 (3)	0.6444 (2)	0.8137 (4)	4.6 (1)	3.8 (1)	2.57 (9)	0.49 (9)	0.02 (9)	0.27 (8)
O(4)	0.6012 (3)	0.3989 (2)	0.7017 (4)	3.7 (1)	4.93 (9)	3.31 (9)	1.52 (8)	0.27 (8)	2.08 (7)
O(5)	0.3210 (3)	0.4510 (3)	0.8971 (4)	4.1 (1)	7.2 (1)	2.89 (9)	0.7 (1)	0.83 (9)	2.19 (9)
C(1)	0.6414 (4)	0.7084 (3)	0.7339 (6)	3.6 (1)	3.5 (1)	3.7 (2)	0.9 (1)	−0.8 (1)	0.4 (1)
C(2)	0.7185 (5)	0.8297 (4)	0.8666 (8)	5.6 (2)	3.5 (2)	6.4 (2)	0.3 (2)	−1.3 (2)	0.2 (2)
C(3)	0.8691 (7)	0.8140 (7)	0.9415 (14)	7.5 (3)	7.9 (3)	17.7 (6)	−1.5 (3)	−6.1 (4)	1.0 (4)
C(4)	0.6396 (10)	0.8713 (7)	1.0537 (14)	17.0 (7)	8.6 (4)	17.4 (7)	−2.9 (5)	6.5 (6)	−6.4 (4)
C(5)	0.7361 (15)	0.9158 (5)	0.7520 (14)	44 (1)	5.0 (2)	14.5 (6)	−8.8 (5)	−13. (7)	4.2 (3)
C(6)	0.6998 (4)	0.3863 (3)	0.5876 (5)	3.3 (1)	3.4 (1)	3.2 (1)	0.8 (1)	−0.7 (1)	0.7 (1)
C(7)	0.8098 (5)	0.3092 (4)	0.6273 (7)	4.9 (2)	5.1 (2)	6.3 (2)	2.0 (1)	−0.6 (2)	2.4 (1)
C(8)	0.7911 (7)	0.2795 (5)	0.8269 (10)	11.5 (3)	12.8 (2)	10.8 (3)	6.8 (2)	1.5 (3)	7.9 (2)
C(9)	0.9598 (7)	0.3731 (7)	0.6293 (15)	4.3 (2)	18.8 (4)	32.3 (7)	2.2 (3)	−0.8 (4)	18.0 (3)
C(10)	0.7685 (10)	0.1919 (6)	0.4629 (14)	22.8 (5)	9.4 (3)	14.5 (6)	11.1 (2)	−6.1 (4)	−1.3 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(OAc)_4(THT)_2$ (2)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	0.08635 (4)	0.05229 (2)	0.01227 (2)	2.32 (2)	2.21 (1)	2.12 (1)	−0.19 (1)	0.01 (1)	−0.02 (1)
S	0.2623 (1)	0.16244 (8)	0.04457 (9)	3.10 (5)	3.31 (5)	3.32 (5)	−0.86 (4)	−0.06 (4)	−0.33 (4)
O(1)	−0.1733 (3)	0.0267 (2)	−0.1042 (2)	3.1 (1)	3.0 (1)	2.9 (1)	−0.0 (1)	−0.4 (1)	0.2 (1)
O(2)	−0.0109 (3)	0.1242 (2)	−0.0832 (2)	3.2 (1)	2.9 (1)	3.2 (1)	−0.3 (1)	−0.6 (1)	0.7 (1)
O(3)	−0.0336 (3)	0.0982 (2)	0.1144 (2)	3.4 (1)	2.9 (1)	2.6 (1)	−0.1 (1)	0.4 (1)	−0.4 (1)
O(4)	0.1960 (3)	−0.0003 (2)	−0.0917 (2)	3.2 (1)	3.3 (1)	2.9 (1)	−0.3 (1)	0.5 (1)	−0.5 (1)
C(1)	−0.1173 (5)	0.0953 (3)	−0.1223 (3)	3.4 (2)	2.9 (2)	2.0 (2)	0.9 (2)	0.3 (2)	−0.1 (2)
C(2)	−0.1803 (6)	0.1469 (3)	−0.1974 (4)	4.1 (2)	4.0 (2)	3.2 (2)	0.7 (2)	−0.2 (2)	0.9 (2)
C(3)	−0.1465 (5)	0.0631 (3)	0.1332 (3)	3.1 (2)	3.1 (2)	2.1 (2)	0.7 (2)	0.2 (2)	0.5 (2)
C(4)	−0.2299 (5)	0.0986 (3)	0.2110 (4)	4.1 (2)	4.5 (2)	2.8 (2)	0.7 (2)	1.0 (2)	−0.4 (2)
C(5)	0.4254 (6)	0.1093 (5)	0.0603 (6)	2.9 (2)	6.7 (3)	8.9 (4)	−0.1 (2)	−1.1 (3)	2.8 (3)
C(6)	0.5187 (8)	0.1447 (6)	−0.0096 (6)	3.8 (3)	10.1 (6)	9.5 (5)	0.1 (4)	1.3 (3)	2.5 (4)
C(7)	0.4438 (7)	0.1692 (6)	−0.0925 (6)	5.3 (3)	12.4 (6)	5.6 (3)	0.3 (4)	1.9 (3)	0.3 (4)
C(8)	0.3093 (6)	0.2094 (4)	−0.0649 (4)	4.6 (3)	5.6 (3)	3.6 (2)	−1.1 (2)	0.5 (2)	1.5 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(OAc)_4(Me_2SO)_2$ (3)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	0.47357 (5)	0.05403 (2)	0.05139 (3)	1.93 (2)	1.72 (2)	2.01 (2)	−0.03 (1)	−0.02 (1)	−0.04 (1)
S	0.4023 (2)	0.16140 (8)	0.15639 (9)	2.35 (6)	2.18 (5)	2.71 (5)	0.01 (5)	0.09 (5)	−0.44 (5)
O(1)	0.6247 (6)	−0.1143 (2)	0.0538 (2)	3.8 (2)	2.6 (1)	2.2 (2)	0.8 (2)	−0.1 (1)	0.1 (1)
O(2)	0.5747 (5)	−0.0138 (2)	0.1506 (3)	3.3 (2)	2.7 (2)	2.8 (2)	0.5 (2)	−0.4 (2)	0.1 (1)
O(3)	0.7419 (5)	−0.0025 (2)	−0.0767 (3)	2.2 (1)	3.0 (2)	3.0 (2)	−0.2 (1)	0.4 (1)	−0.2 (1)
O(4)	0.6928 (5)	0.0983 (2)	0.0199 (3)	2.6 (2)	2.7 (2)	3.4 (2)	−0.7 (1)	0.1 (2)	−0.2 (1)
O(5)	0.5115 (5)	0.2274 (3)	0.1803 (3)	2.9 (2)	2.6 (2)	4.7 (2)	−0.5 (2)	−0.1 (2)	−0.8 (2)
C(1)	0.6295 (7)	−0.0825 (3)	0.1303 (4)	1.8 (2)	2.3 (2)	3.1 (2)	−0.0 (2)	0.2 (2)	0.6 (2)
C(2)	0.7037 (8)	−0.1296 (4)	0.2076 (4)	4.0 (3)	3.8 (3)	2.7 (2)	1.4 (2)	0.1 (2)	1.2 (2)
C(3)	0.7794 (8)	0.0622 (3)	−0.0357 (4)	2.3 (3)	2.5 (2)	2.9 (2)	−0.1 (2)	−0.4 (2)	0.6 (2)
C(4)	0.9426 (8)	0.0952 (4)	−0.0553 (4)	2.6 (3)	3.9 (3)	4.0 (3)	−1.0 (2)	0.4 (2)	0.7 (2)
C(5)	0.2169 (8)	0.2043 (4)	0.1193 (4)	2.6 (3)	4.4 (3)	3.8 (3)	0.8 (2)	−0.7 (2)	−1.2 (2)
C(6)	0.3398 (9)	0.1154 (4)	0.2594 (4)	4.3 (3)	4.0 (3)	2.7 (2)	−0.3 (3)	1.2 (2)	−0.2 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table I. No effort was made to locate the hydrogen atoms. The final difference Fourier map showed no significant residual electron density.

X-ray data for $Rh_2(OAc)_4(Me_2SO)_2$ (**3**) were also collected in the orthorhombic crystal system. Systematic absences uniquely determined the space group as *Pbca*: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$. With only four formula weights in the unit cell the structure was required to be located on an inversion center. A Patterson map revealed the position of the Rh atom which was about an inversion center at $(^1/_2, 0, 0)$. Three cycles of least-squares refinement of the Rh atom position followed by a difference Fourier map led to the location of the remaining 12 atoms in the complex. The structure was further refined to convergence with anisotropic thermal parameters for all 13 atoms. Hydrogen atoms were not included in the refinement and the final residuals and largest peak in the final difference Fourier map are summarized in Table I.

Tables of observed and calculated structure factors are available as supplementary material.

Results

The positional and thermal parameters for the three compounds are compiled in Tables II–IV and the bond distances and angles are given in Tables V–VII. Each structure refined to relatively low discrepancy indices and is represented by the general formula $Rh_2(O_2CR)_4L_2$ with no additional solvate molecules. A description of the prominent features of each structure will now be given.

$Rh_2(piv)_4(H_2O)_2$ (1). This compound crystallizes in the triclinic space group $P\bar{1}$ with one formula weight in the unit cell. Four pivalate groups bridge the dirhodium(II) unit which

Table V. Bond Distances (Å) and Angles (Deg) for $Rh_2(piv)_4(H_2O)_2$ (**1**)

Distances			
Rh–Rh′	2.371 (1)	O(4)–C(6)	1.268 (4)
Rh–O(1)	2.036 (2)	C(1)–C(2)	1.504 (4)
Rh–O(2)	2.036 (2)	C(2)–C(3)	1.531 (7)
Rh–O(3′)	2.043 (2)	C(2)–C(4)	1.552 (10)
Rh–O(4′)	2.044 (2)	C(2)–C(5)	1.453 (9)
Rh–O(5)	2.295 (2)	C(6)–C(7)	1.543 (4)
O(1)–C(1)	1.243 (4)	C(7)–C(8)	1.544 (8)
O(2)–C(6)	1.248 (4)	C(7)–C(9)	1.484 (8)
O(3)–C(1)	1.282 (4)	C(7)–C(10)	1.506 (8)
Angles			
Rh′–Rh–O(1)	87.73 (7)	O(1)–C(1)–O(3)	124.9 (3)
Rh′–Rh–O(2)	88.29 (7)	O(1)–C(1)–C(2)	118.1 (3)
Rh′–Rh–O(3′)	88.54 (7)	O(3)–C(1)–C(2)	117.0 (3)
Rh′–Rh–O(4′)	87.99 (7)	C(1)–C(2)–C(3)	106.4 (3)
Rh′–Rh–O(5)	179.76 (7)	C(1)–C(2)–C(4)	110.9 (4)
O(1)–Rh–O(2)	92.3 (1)	C(1)–C(2)–C(5)	110.3 (4)
O(1)–Rh–O(3′)	176.12 (7)	C(3)–C(2)–C(4)	107.3 (6)
O(1)–Rh–O(4′)	88.4 (1)	C(3)–C(2)–C(5)	108.7 (7)
O(1)–Rh–O(5)	92.49 (9)	C(4)–C(2)–C(5)	112.9 (8)
O(2)–Rh–O(3′)	88.6 (1)	O(2)–C(6)–O(4)	125.7 (3)
O(2)–Rh–O(4′)	176.17 (7)	O(2)–C(6)–C(7)	117.1 (3)
O(2)–Rh–O(5)	91.61 (9)	O(4)–C(6)–C(7)	117.1 (3)
O(3′)–Rh–O(4′)	90.4 (1)	C(6)–C(7)–C(8)	110.4 (4)
O(3′)–Rh–O(5)	91.24 (9)	C(6)–C(7)–C(9)	109.9 (4)
O(4′)–Rh–O(5)	92.11 (9)	C(6)–C(7)–C(10)	105.8 (3)
Rh–O(1)–C(1)	120.5 (2)	C(8)–C(7)–C(9)	111.0 (5)
Rh–O(2)–C(6)	119.2 (2)	C(8)–C(7)–C(10)	106.6 (5)
Rh–O(3′)–C(1′)	118.3 (2)	C(9)–C(7)–C(10)	113.0 (7)
Rh–O(4′)–C(6′)	118.6 (2)		

Table VI. Bond Distances (Å) and Angles (Deg) for $Rh_2(OAc)_4(THT)_2$ (**2**)

Distances			
Rh–Rh′	2.413 (1)	O(2)–C(1′)	1.275 (6)
Rh–S	2.517 (1)	O(3)–C(3)	1.272 (6)
Rh–O(1)	2.035 (3)	O(4)–C(3′)	1.274 (6)
Rh–O(2)	2.046 (3)	C(1)–C(2)	1.508 (6)
Rh–O(3)	2.036 (3)	C(3)–C(4)	1.512 (6)
Rh–O(4)	2.042 (3)	C(5)–C(6)	1.484 (10)
S–C(5)	1.827 (6)	C(6)–C(7)	1.469 (12)
S–C(8)	1.825 (5)	C(7)–C(8)	1.522 (9)
O(1)–C(1)	1.261 (5)		
Angles			
Rh′–Rh–S	177.55 (4)	Rh–S–C(8)	107.5 (2)
Rh′–Rh–O(1)	87.48 (9)	C(5)–S–C(8)	94.7 (3)
Rh′–Rh–O(2)	88.06 (9)	Rh–O(1)–C(1)	120.2 (3)
Rh′–Rh–O(3)	87.49 (9)	Rh–O(2)–C(1′)	118.7 (3)
Rh′–Rh–O(4)	88.29 (9)	Rh–O(3)–C(3)	119.9 (3)
S–Rh–O(1)	91.68 (9)	Rh–O(4)–C(3′)	118.8 (3)
S–Rh–O(2)	92.80 (9)	O(1)–C(1)–C(2′)	125.5 (4)
S–Rh–O(3)	90.19 (9)	O(1)–C(1)–C(2)	117.1 (4)
S–Rh–O(4)	94.03 (9)	O(2′)–C(1)–C(2)	117.4 (4)
O(1)–Rh–O(2)	175.5 (1)	O(3)–C(3)–O(4′)	125.5 (4)
O(1)–Rh–O(3)	89.2 (1)	O(3)–C(3)–C(4)	117.7 (4)
O(1)–Rh–O(4)	90.6 (1)	O(4′)–C(3)–C(4)	116.8 (4)
O(2)–Rh–O(3)	91.4 (1)	S–C(5)–C(6)	105.8 (5)
O(2)–Rh–O(4)	88.5 (1)	C(5)–C(6)–C(7)	111.2 (6)
O(3)–Rh–O(4)	175.8 (1)	C(6)–C(7)–C(8)	109.2 (6)
Rh–S–C(5)	107.1 (2)	S–C(8)–C(7)	106.0 (5)

is located about a crystallographic center of inversion. Two oxygen atoms of water molecules coordinate to the Rh atoms via the axial positions with Rh–O distances of 2.295 (2) Å and a view of the molecule is given in Figure 1 with the atom numbering scheme. The Rh–Rh bond is relatively short with a length of 2.371 (1) Å. Selected structural parameters for **1**–**3** and several other representative $Rh_2(O_2CR)_4L_2$ complexes are tabulated in Table VIII.

$Rh_2(OAc)_4(THT)_2$ (2). The structure consists of the familiar tetraacetate framework about the dirhodium(II) unit with a THT molecule binding into each axial position giving a Rh–S distance of 2.517 (1) Å. The molecule is located on an inversion center with a Rh–Rh bond length of 2.413 (1) Å. A view of **2** is presented in Figure 2 with the atom labeling scheme.

Table VII. Bond Distances (Å) and Angles (Deg) for $Rh_2(OAc)_4(Me_2SO)_2$ (**3**)

Distances			
Rh–Rh′	2.406 (1)	S–C(6)	1.789 (5)
Rh–S	2.451 (1)	O(1)–C(1)	1.255 (6)
Rh–O(1′)	2.032 (3)	O(2)–C(1)	1.273 (6)
Rh–O(2)	2.043 (3)	O(3)–C(3)	1.281 (7)
Rh–O(3′)	2.035 (4)	O(4)–C(3)	1.254 (7)
Rh–O(4)	2.035 (3)	C(1)–C(2)	1.524 (6)
S–O(5)	1.477 (5)	C(3)–C(4)	1.503 (6)
S–C(5)	1.797 (5)		
Angles			
Rh′–Rh–S	176.42 (4)	Rh–S–C(5)	107.9 (2)
Rh′–Rh–O(1′)	87.74 (9)	Rh–S–C(6)	107.4 (2)
Rh′–Rh–O(2)	87.89 (9)	O(5)–S–C(5)	108.1 (2)
Rh′–Rh–O(3′)	87.83 (9)	C(5)–S–C(6)	107.3 (2)
Rh′–Rh–O(4)	87.82 (9)	C(5)–S–C(6)	100.4 (3)
S–Rh–O(1′)	91.49 (9)	Rh–O(1′)–C(1′)	119.8 (3)
S–Rh–O(2)	92.85 (9)	Rh–O(2)–C(1)	118.7 (3)
S–Rh–O(3′)	88.67 (9)	Rh–O(3′)–C(3′)	119.2 (3)
S–Rh–O(4)	95.68 (9)	Rh–O(4)–C(3)	119.8 (3)
O(1′)–Rh–O(2)	175.6 (1)	O(1)–C(1)–O(2)	125.8 (4)
O(1′)–Rh–O(3′)	89.6 (1)	O(1)–C(1)–C(2)	118.3 (4)
O(1′)–Rh–O(4)	90.5 (1)	O(2)–C(1)–C(2)	115.8 (4)
O(2)–Rh–O(3′)	89.9 (1)	O(3)–C(3)–O(4)	125.3 (5)
O(2)–Rh–O(4)	89.6 (1)	O(3)–C(3)–C(4)	116.2 (5)
O(3′)–Rh–O(4)	175.6 (1)	O(4)–C(3)–C(4)	118.4 (5)
Rh–S–O(5)	123.3 (2)		

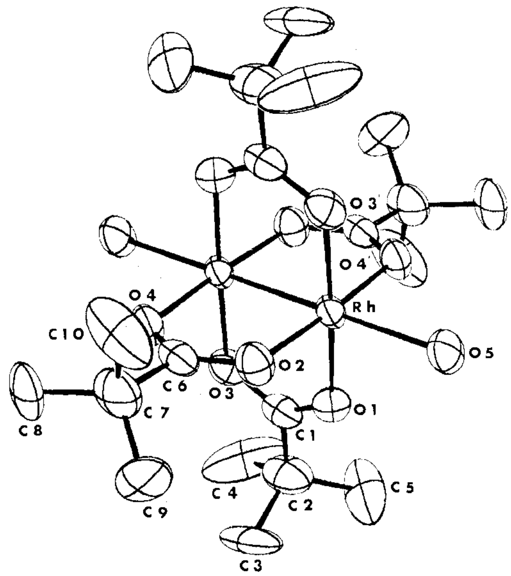

Figure 1. An ORTEP drawing of $Rh_2(piv)_4(H_2O)_2$ (**1**) showing the atom labeling scheme. The molecule is located about an inversion center. Thermal ellipsoids have been scaled so as to enclose 50% of their electron density except the methyl carbon atoms of the pivalate groups which have been arbitrarily reduced in size for clarity.

$Rh_2(OAc)_4(Me_2SO)_2$ (3). The structure of this compound is quite similar to **2**. The molecule is again located on an inversion center with four bridging acetate groups and a Rh–Rh distance of 2.406 (1) Å. The Me_2SO molecule coordinates through the sulfur atoms with a Rh–S distance of 2.451 (1) Å. A view of **3** with the atom labeling scheme is given in Figure 3.

Discussion

Table VIII provides a listing of various structural parameters for one pivalate, one carbonate, and six acetate complexes of dirhodium(II). The data show that throughout the series only the Rh–Rh and Rh–L distances vary significantly. The Rh–O

Table VIII. Selected Structural Parameters for Some $Rh_2(O_2CR)_4L_2$ Compounds

R	L	Rh-Rh, Å	Rh-L, Å	Rh-O, Å	O-C-O, deg	ref
CMe_3	H_2O	2.371 (1)	2.295 (2)	2.039 (2)	125.3 (3)	this work
O^{-} [a]	H_2O	2.378 (1)	2.344 (5)	2.033 (4)	122.6 (6)	15
CH_3	H_2O	2.3855 (5)	2.310 (3)	2.039 (8)	124.8 (3)	7
CH_3	py	2.3963 (2)	2.227 (3)	2.039 (2)	125.7 (1)	8
CH_3	Me_2SO	2.406 (1)	2.451 (1)	2.036 (3)	125.5 (5)	this work
CH_3	THT	2.413 (1)	2.517 (1)	2.040 (3)	125.5 (4)	this work
CH_3	CO	2.4193 (3)	2.091 (3)	2.032 (2)	125.5 (2)	10
CH_3	PPh_3	2.449 (2)	2.479 (3)	2.044 (4)	126.4 (4)	16

[a] In $Cs_4[Rh_2(CO_3)_4(H_2O)_2]\cdot 6H_2O$.

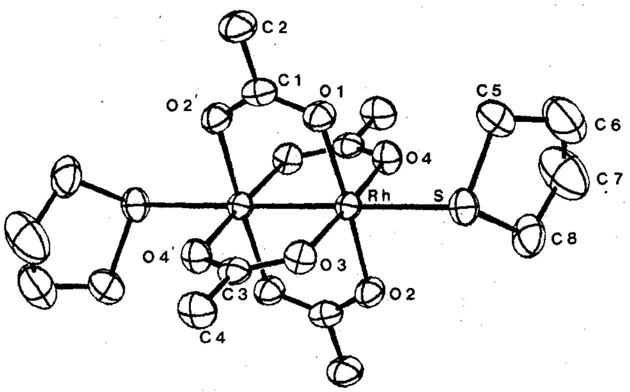

Figure 2. An ORTEP plotting of $Rh_2(OAc)_4(THT)_2$ (**2**) with the atom labeling scheme given. The molecule is located about a crystallographic center of inversion. Vibrational ellipsoids are drawn at the 50% probability level.

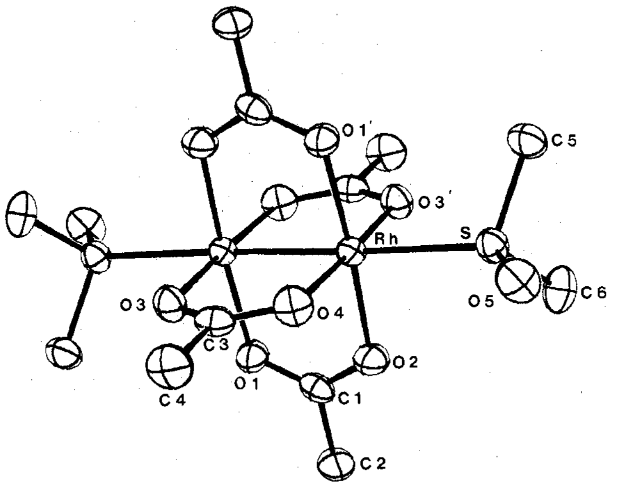

Figure 3. An ORTEP view of the $Rh_2(OAc)_4(Me_2SO)_2$ molecule, **3**, using 50% probability ellipsoids and showing the atom labeling scheme. A center of inversion is located at the midpoint of the Rh–Rh bond.

distances are essentially constant for all eight compounds. The O–C–O angles are all in the range 125.5 ± 1.0° except for the carbonate complex $Cs_4[Rh_2(CO_3)_4(H_2O)_2]\cdot 6H_2O$[15] for which the decreased O–C–O angle (122.6 (6)°) may simply reflect the greater rigidity of the carbonate unit compared to acetate. In the table the eight compounds are arranged in order of increasing Rh–Rh bond length and several trends are evident. The enhanced electron-donating ability of the pivalate and carbonate ligands leads to shorter Rh–Rh distances than for the acetate complex when H_2O is the axial ligand. The pivalate compound, **1**, has the shortest Rh–Rh distance yet discovered for any dirhodium(II) tetracarboxylate. Better σ-donating ligands lead to longer Rh–Rh distances but the net effect is a function of the π-accepting ability as well. Thus, very good π-acceptor ligands like CO are more effective in lengthening the Rh–Rh bond than nitrogen- or sulfur-donor ligands but not as much as phosphorus donor ligands such as PPh_3[16] which possess both good σ-donating and good π-accepting characteristics.

The similarity of the molecular structures of $Rh_2(piv)_4(H_2O)_2$ and $Rh_2(OAc)_4(H_2O)_2$[7] invites a consideration of the factors which would account for the roughly 0.015 Å variation in Rh–Rh bond length. Electrochemical[17] and theoretical[18] data provide some insights into the possible effects of carboxylate R group substituents on the electronic structure. The half-wave oxidation potentials ($E_{1/2}$) have been found to correlate[17] with the nature of the R substituent in a series of $Rh_2(O_2CR)_4$ complexes. Highly electron-donating substituents such as CMe_3 destabilize the complex toward oxidation and thus lower the energy of the highest occupied molecular orbital (HOMO). SCF-Xα-SW calculations on $Rh_2(O_2CH)_4(H_2O)_2$ show[18] that the primarily oxygen molecular orbitals of the formate ligands are located between the primarily Rh 4d orbitals. These metal orbitals, however, have significant ligand character and it is difficult to sort out explicitly the effect of increasing the electron-donating character of the R group. It would seem that the shift in $E_{1/2}$ values to lower energies with increasing the R group electron-donor character should correspond to an overall lowering of the Rh 4d orbital energies and, consequently, a shortening of the Rh–Rh bond. The basic orbital configuration in dirhodium(II) systems[18] is $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$ and the combination of appreciable metal–ligand orbital mixing and an antibonding HOMO makes predictions of carboxylate substituent effects on the Rh–Rh bond lengths somewhat problematic.

Both of the sulfur-donor ligands appear to have close to the same effect on the Rh–Rh bond length despite the differences in the nature of the coordinating sulfur atom. The THT complex **2** has a slightly longer (0.006 Å) Rh–Rh bond but also a longer Rh–S bond. The Rh–S distance of 2.517 (1) Å is nearly the same as the Rh–S axial distance of 2.521 (5) Å in $Rh_2(OSCCH_3)_4(CH_3CSOH)_2$[19] in which the axial thioacetic acid moiety is found coordinated in the thione form. The Rh–Rh bond (2.550 (3) Å) in this thioacetic acid complex is significantly longer than any of the carboxylates in Table VIII and illustrates the predominant effect on the bridging ligand characteristics over those of the axial ligand in determining the Rh–Rh bond length.

Adducts between Me_2SO and various $Rh_2(O_2CR)_4$ complexes have been part of several investigations[17,20-25] since the

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first report of $Rh_2(OAc)_4(Me_2SO)_2$ in 1963 by Johnson, Hunt, and Neumann.[20] These authors proposed that Me_2SO coordinated through the sulfur atom on the basis of the orange color of the adduct (oxygen-ligated adducts were recognized to be green to blue-green) and the position of the S–O stretching frequency (1086 cm^{-1}) in the infrared spectrum. The latter observation was known[26] to be diagnostic of metal–sulfur bonding since the S–O stretching frequency exceeded that of the free ligand (1055 cm^{-1}). These stretching frequencies are consistent with the S–O distances as determined by X-ray crystallography. In Me_2SO itself the S–O bond length is 1.513 (5) Å[27] whereas in $Rh_2(OAc)_4(Me_2SO)_2$ the distance has decreased to 1.477 (5) Å. In $PdCl_2(Me_2SO)_2$, for example, where Pd–S bonding has been found, the S–O distance is 1.475 (5) Å[28] (ν(S–O stretch) = 1116 cm^{-1}). Very strong bonding to the sulfur as in the $(CH_3)_3SO^+$ ion leads to a still shorter S–O distance[29,30] (1.45 (1) Å) and a higher S–O stretching frequency[26] (1233 cm^{-1}), as expected.

The Rh–S distance of 2.451 (1) Å in **3** clearly demonstrates the influence of the trans effect of the Rh–Rh bond on the bond length. Normal Rh–S bond lengths are in the range 2.23–2.26 Å as found in $Rh_2(OSCCH_3)_4(CH_3CSOH)_2$[19] and *fac*-$RhCl_3(Me_2SO)_3$.[31] The latter complex with Rh(III) has only two Me_2SO molecules coordinating through the sulfur atom. The Rh–S distance in $Rh_2(OAc)_4(Me_2SO)_2$ (**2**) is shorter by nearly 0.07 Å than in the THT adduct **3** and this would point to the presence of greater π back-bonding interactions in **2** as has been suggested previously from evaluation of thermodynamic data.[25]

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Registry No. 1, 70084-27-4; **2**, 72207-18-2; **3**, 26023-60-9; $Rh_2(OAc)_4$, 15956-28-2.

Supplementary Material Available: Tables of observed and calculated structure factors for the three compounds (25 pages). Ordering information is given on any current masthead page.

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Pyridine and Pyrazine Adducts of Tetrakis(acetato)dichromium

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Pyridine and pyrazine form 2:1 and 1:1 adducts, respectively, with $Cr_2(OAc)_4$ which have been characterized by X-ray crystallography. The structures are isomorphous to those of the corresponding copper(II) complexes. Crystals of $Cr_2(OAc)_4(py)_2$ (**1**) are orthorhombic and belong to space group *Pbca* with four molecules in a unit cell of dimensions a = 13.055 (2) Å, b = 8.645 (1) Å, c = 19.560 (3) Å, and V = 2207.5 (6) Å^3. The structure was refined with 891 reflections having $I > 3\sigma(I)$ to final discrepancy indices of R_1 = 0.060 and R_2 = 0.081. The structure consists of centrosymmetric formula units with a Cr–Cr bond length of 2.369 (2) Å and a Cr–N bond length of 2.335 (5) Å. The pyrazine (pyz) adduct, $Cr_2(OAc)_4(pyz)$ (**2**), crystallizes in the space group *C*2/*m* with a = 7.979 (2) Å, b = 14.350 (4) Å, c = 7.376 (2) Å, β = 101.78 (2)°, V = 826.7 (4) Å^3, and Z = 2. The structure was solved by using 365 reflections with $I > 2\sigma(I)$ to give final residuals of R_1 = 0.065 and R_2 = 0.079. The Cr–Cr bond length in the $Cr_2(OAc)_4$ units is 2.295 (5) Å and these centrosymmetric units are linked into linear chains by the pyrazine molecules with C–N bond lengths of 2.31 (1) Å.

Introduction

Dichromium(II) complexes are of interest because of the extraordinary variation in the Cr–Cr bond length.[1] The range extends from 1.828 (2) Å in tetrakis(2-methoxy-5-methylphenyl)dichromium(II)[2] to 2.541 (1) Å in $Cr_2(O_2CCF_3)_4(Et_2O)_2$.[3] The distribution of the Cr–Cr bond lengths has been bimodal with the carboxylates constituting an upper range (2.28–2.54 Å) and most of the others falling between the value of 1.98 Å in $[Cr_2(CH_3)_8]^{4-}$[4] and the aforementioned 1.828 Å. The existence of Cr–Cr bonds of order 4 is universally accepted for the species in the lower range, but controversy[5] has arisen concerning those in the upper range. However, the existence of weak quadruple bonds in the carboxylato compounds has been supported by the results of SCF–Xα–SW calculations[6] and Hartree–Fock calculations in which at least partial account of electron correlation has been included.[7] The latter calculations suggest that the curve of energy vs. Cr–Cr distance for a $Cr_2(O_2CR)_4$ system is very shallow and thus, at least in part, allow us to understand the extreme sensitivity of Cr–Cr bond length to the identities of R and L in the $Cr_2(O_2CR)_4L_2$ compounds.[3] However, no neat, unambiguous relationships have yet been found and consequently efforts have continued

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