I. This effect explains the relative positions of the Fe, C(4), and C(5) atoms, and the same effect is observed in complex **3**, also. A crude molecular model reveals that a structure having a planar chelate ring can be formed only with imposing considerable ring strain and that the shortest intramolecular contact distance between the iron and boron portions of the molecule is a F···H (C_5H_5) contact of ca. 3.1 Å.

The second geometrical isomer observed for **4** in solution is, presumably, the other boat isomer where the η^5-C_5H_5 ligand and the fluorine atom are in closest proximity. Although a chair conformation is possible, also, there has been no evidence of such a structure for metalla-β-diketonate chelate rings.

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Ambidentate Character of Dimethyl Sulfoxide in Adducts of Tetrakis(propionato)- and Tetrakis(trifluoroacetato)dirhodium(II)

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Dimethyl sulfoxide forms 2:1 adducts with rhodium(II) carboxylates to give compounds having the general formula $Rh_2(O_2CR)_4(Me_2SO)_2$. The structures of two compounds of this type have been determined by using single-crystal X-ray diffraction techniques, and the results reveal that oxygen or sulfur atom coordination of Me_2SO to $Rh_2(O_2CR)_4$ is dependent on the nature of the carboxylate R group substituent. Compound **1**, $Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$, crystallizes as orange prisms in the space group $P2_1/n$ with four molecules in a cell of dimensions $a = 9.057$ (2) Å, $b = 15.709$ (4) Å, $c = 18.164$ (2) Å, and $\beta = 101.62$ (1)°. The structure was refined by using 3244 data with $I > 3\sigma(I)$ to an R_1 value of 0.045. There is no crystallographically imposed symmetry on the dinuclear unit; four propionate groups bridge the rhodium atoms, and two Me_2SO molecules are coordinated through their sulfur atoms in the axial positions just as in the corresponding acetate complex whose structure has been previously determined. The Rh–Rh bond length is 2.407 (1) Å with an average Rh–S distance of 2.449 (1) Å. Compound **2**, $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, crystallizes as dark blue needles in the space group $P\bar{1}$ with one formula weight in a cell with $a = 8.621$ (2) Å, $b = 9.500$ (2) Å, $c = 8.766$ (2) Å, $\alpha = 112.68$ (1)°, $\beta = 110.99$ (2)°, and $\gamma = 87.83$ (2)°. A total of 1984 reflections with $I > 3\sigma(I)$ were used to refine the structure to a final R_1 value of 0.042. The structure consists of a dirhodium(II) moiety with a Rh–Rh bond length of 2.419 (1) Å bridged by four trifluoroacetate groups and two axial oxygen-bonded Me_2SO molecules with a Rh–O distance of 2.236 (3) Å. A crystallographic inversion center is located at the midpoint of the Rh–Rh bond. The observed ν_{SO} values in the infrared spectra for these compounds are in accord with long-established spectroscopic criteria for O- and S-bonded metal–sulfoxide complexes.

Introduction

A considerable amount of work has now been reported on the chemical and structural properties of complexes of Rh_2^{4+}, especially those with bridging carboxylato ligands.[1] These have the general formula $Rh_2(O_2CR)_4L_2$, where the L groups are monodentate ligands bound in each of the axial positions. One of these compounds, whose structure we recently reported,[1] is $Rh_2(O_2CCH_3)_4(Me_2SO)_2$, and it was found that the dimethyl sulfoxide (Me_2SO) ligands are attached to the rhodium atoms through their sulfur atoms. This is consistent with the inference made on the basis of spectral data (ν_{SO} = 1086 cm^{-1}) by Johnson, Hunt, and Neumann in 1963 when they reported the compound for the first time.[2]

The characteristic ligand properties of Me_2SO and other sulfoxides were first reported, with extensive documentation, about 20 years ago.[3,4] The ambidentate character of Me_2SO was explicitly noted, and the utility of infrared spectra in distinguishing between O- and S-bonded ligands was discussed and illustrated. It was shown that, for most of the transition-metal ions and main-group acceptors, coordination occurs through the oxygen atoms of Me_2SO and other sulfoxides but that, for Pd^{II} and Pt^{II}, coordination through the sulfur atom was indicated by an upward shift of ν_{SO}. These correlations were subsequently confirmed by X-ray crystallography.[5-7]

This paper reports the structures of two 2:1 adducts of rhodium(II) carboxylates with Me_2SO. Compound **1**, $Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$, was first prepared and characterized by Mal'kova and Shafranskii.[8] Their results suggest that the complex is quite analogous to the corresponding acetate compound.[1,2] The interaction of Me_2SO with $Rh_2(O_2CCF_3)_4$ was reported several years ago by Kitchens and Bear[9] to produce a blue solution (neat Me_2SO) which, upon removal of excess Me_2SO, gave them a "green tar-like substance" that they regarded as "not a true adduct as in the case of rhodium(II) acetate". Kitchens and Bear noted that this product is most

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Table I. Crystallographic Parameters

parameter	1	2
space group	$P2_1/n$	$P\bar{1}$
a, Å	9.057 (2)	8.621 (2)
b, Å	15.709 (4)	9.500 (2)
c, Å	18.164 (2)	8.766 (2)
α, deg	90.0	112.68 (1)
β, deg	101.62 (1)	110.99 (2)
γ, deg	90.0	87.83 (2)
V, Å	2531 (1)	614.2 (5)
d_{calcd}, g/cm^3	1.72	2.20
Z	4	1
formula wt	654.37	814.14
cryst size, mm	0.25 × 0.27 × 0.45	0.15 × 0.20 × 0.35
μ(Mo Kα), cm^{-1}	14.705	16.159
range 2θ, deg	4–50	4–50
no. unique data	3493	2159
no. data, $F_o^2 > 3\sigma(F_o^2)$	3244	1984
no. variables	271	172
R_1	0.045	0.042
R_2	0.068	0.070
esd	1.857	1.897
largest peak, e/Å^3 ^{a}	0.44	0.55

^{a} Largest peak in the final difference Fourier map.

likely a result of decomposition of the tetracarboxylate framework but that the initial blue solution could be indicative of axially O-bonded Me_2SO. We have found that by avoiding prolonged exposure of $Rh_2(O_2CCF_3)_4$ to excess Me_2SO, it is possible to isolate and crystallographically characterize in detail a crystalline, dark blue solid having the composition $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, which we shall designate as compound **2**.

Experimental Section

Compound Preparation. Rhodium(II) propionate and trifluoroacetate were prepared by using a procedure given by Kitchens and Bear.[9] The compounds were isolated in their hydrated forms. Both are readily converted to the anhydrous forms by heating at ca. 150 °C for 30 min.

$Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$, **1**, was prepared by dissolving $Rh_2(O_2CC_2H_5)_4(H_2O)_2$ in ca. 4 mL of 1:1 H_2O–Me_2SO and evaporating the resulting orange solution. The compound crystallized as orange prisms.

$Rh_2(O_2CCF_3)_4(Me_2SO)_2$, **2**, was prepared by dissolving $Rh_2(O_2CCF_3)_4$ in a 1:1 solution of chloroform and benzene containing ca. 0.5 mL of Me_2SO. The solution was evaporated to yield a microcrystalline, blue solid which was recrystallized from a 1:1 chloroform–benzene mixture. Prolonged (ca. 1 week) exposure to excess Me_2SO eventually yields an orange solution indicative of degradation of the tetracarboxylate framework as noted in previous work.[9] Compound **2** crystallized as dichroic, dark blue crystals which appear red in some orientations when viewed with transmitted light.

X-ray Crystallography. Collection of Data. Crystals of **1** and **2** were coated with epoxy resin and mounted on a glass fiber. Crystals of **2** were found to lose Me_2SO if not protected with epoxy cement. Data were collected for both compounds on an Enraf-Nonius CAD-4F diffractometer at 26 ± 1 °C using Mo Kα radiation (λ = 0.71073 Å) with a graphite-crystal monochromator in the incident beam. A summary of data collection and refinement parameters is presented in Table I. The final lattice constants for both compounds were obtained from a least-squares fit to 25 reflections in the range 24° $< 2\theta <$ 37°. Other details concerning the collection and processing of data have appeared before.[10] Diffraction data were corrected for Lorentz and polarization effects, but corrections for absorption were deemed unnecessary in view of the small absorption coefficients (Table I).

Solution and Refinement of the Structures.[11] Data for $Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$, **1**, were collected for a monoclinic crystal system. The observed volume was consistent with $Z = 4$. Examination of the data revealed systematic absences for $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, which uniquely determine the space group as $P2_1/n$. The positions of the two independent Rh atoms were determined from a three-dimensional Patterson function. Three cycles of least-squares refinement of the atomic positional and thermal parameters gave discrepancy indices of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.39$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2} = 0.47$. Subsequent difference Fourier maps followed by least-squares refinement located all 30 nonhydrogen atoms in the dinuclear unit. Anisotropic thermal parameters were assigned to all 30 atoms, and the structure refined to the final discrepancy factors listed in Table I. The largest shift/error ratio in the last least-squares cycle was 0.21. A final difference map showed the five highest peaks (0.30–0.44 e/Å^3) to be in the vicinity of the terminal propionate carbon atoms: C(3), C(6), C(9), and C(12). Hydrogen atoms were omitted from the refinement.

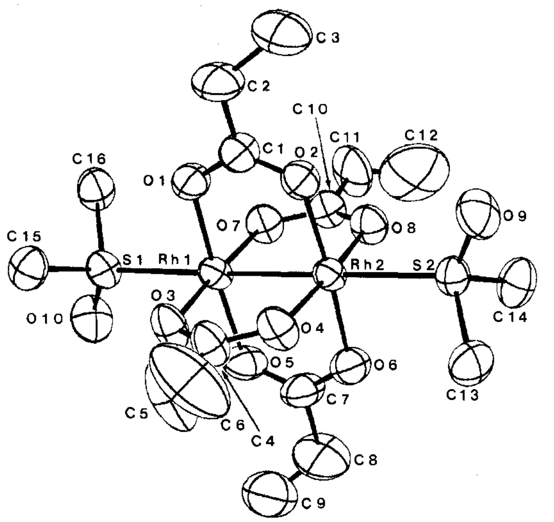

Figure 1. ORTEP drawing of $Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$, **1**, with thermal ellipsoids drawn at the 40% probability level.

Crystals of $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, **2**, were found to be triclinic. The cell volume was consistent with $Z = 1$. Solution and refinement were undertaken in space group $P\bar{1}$. A three-dimensional Patterson function gave the position of the Rh atom as the highest peak. Three cycles of least-squares refinement followed by a difference Fourier map revealed the positions of the remaining 18 atoms in the asymmetric unit. Anisotropic temperature factors were assigned to all 19 atoms, and the structure refined to convergence in $P\bar{1}$. The largest shift/error ratio in the last least-squares cycle was 0.04. The methyl hydrogen atoms of the Me_2SO were not included. Final residuals and the magnitude of the largest peak in the final difference map are given in Table I.

Tables of observed and calculated structure factor amplitudes with $I > 3\sigma(I)$ for **1** and **2** are available as supplementary material.

Results

Tables II and III record the positional and thermal parameters for **1** and **2**, respectively. Bond distances and angles are compiled in Tables IV and V. The structures are both represented by the general formula $Rh_2(O_2CR)_4(Me_2SO)_2$ with no solvent of crystallization molecules. A detailed description of each structure will now be given.

$Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$, 1. Four molecules of **1** occupy general positions in the unit cell with no crystallographically imposed symmetry. The structure, illustrated in Figure 1, consists of four propionate ligands bridging the Rh_2^{4+} unit with a Rh–Rh bond distance of 2.407 (1) Å. The axial positions contain two Me_2SO molecules coordinated through the sulfur atoms with Rh(1)–S(1) and Rh(2)–S(2) distances of 2.453 (1) and 2.445 (1) Å, respectively. The Rh–Rh–S chains are essentially linear with values of 178.30 (3) and 179.52 (3)° for the angles at Rh(1) and Rh(2), respectively. The carboxylate oxygen atoms form a square plane about each Rh atom with each Rh atom displaced 0.08 Å out of the plane toward the axial Me_2SO molecules. As can be seen from

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

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$ (1)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	0.49350 (5)	0.02083 (3)	0.29937 (2)	5.13 (2)	3.28 (2)	3.70 (2)	0.29 (2)	0.38 (2)	0.21 (1)
Rh(2)	0.51871 (5)	0.13325 (3)	0.21269 (2)	4.73 (2)	3.44 (2)	3.64 (2)	0.09 (2)	0.66 (2)	0.12 (1)
S(1)	0.4597 (2)	−0.0937 (1)	0.38627 (8)	5.91 (7)	4.22 (6)	4.61 (6)	0.81 (6)	1.17 (6)	0.49 (5)
S(2)	0.5461 (2)	0.2468 (1)	0.12433 (8)	5.58 (7)	4.23 (6)	4.72 (6)	−0.04 (6)	1.49 (5)	0.61 (6)
O(1)	0.2729 (4)	0.0116 (3)	0.2496 (2)	4.7 (2)	5.7 (2)	5.4 (2)	−0.3 (2)	0.3 (2)	1.1 (2)
O(2)	0.2971 (4)	0.1168 (3)	0.1678 (2)	5.1 (2)	5.6 (2)	5.0 (2)	0.3 (2)	0.4 (2)	1.3 (2)
O(3)	0.4418 (5)	0.1117 (2)	0.3692 (2)	10.2 (3)	3.8 (2)	4.4 (2)	0.5 (2)	2.7 (2)	−0.1 (1)
O(4)	0.4631 (5)	0.2155 (3)	0.2892 (2)	8.4 (2)	4.0 (2)	4.7 (2)	0.7 (2)	1.6 (2)	−0.2 (1)
O(5)	0.7150 (5)	0.0387 (3)	0.3445 (2)	5.8 (2)	5.9 (2)	6.0 (2)	0.1 (2)	−1.2 (2)	0.9 (2)
O(6)	0.7376 (5)	0.1444 (3)	0.2636 (2)	5.6 (2)	5.9 (2)	6.2 (2)	−0.8 (2)	0.2 (2)	0.8 (2)
O(7)	0.5475 (5)	−0.0624 (3)	0.2237 (2)	7.3 (2)	3.8 (2)	5.4 (2)	0.2 (2)	1.7 (2)	−0.3 (2)
O(8)	0.5743 (5)	0.0418 (3)	0.1432 (2)	6.9 (2)	4.9 (2)	5.1 (2)	0.1 (2)	1.9 (2)	−0.5 (2)
O(9)	0.4139 (5)	0.2740 (3)	0.0660 (3)	7.0 (2)	8.6 (3)	6.7 (2)	1.2 (2)	0.9 (2)	2.8 (2)
O(10)	0.5921 (5)	−0.1271 (3)	0.4375 (3)	6.8 (2)	7.9 (3)	7.2 (2)	2.8 (2)	1.3 (2)	2.5 (2)
C(1)	0.2215 (7)	0.0625 (4)	0.1932 (3)	5.2 (3)	5.0 (3)	5.8 (3)	0.3 (3)	0.9 (2)	0.6 (3)
C(2)	0.0572 (8)	0.0561 (5)	0.1597 (4)	5.2 (3)	9.0 (5)	7.7 (4)	0.1 (3)	−1.2 (3)	1.2 (4)
C(3)	0.0215 (10)	0.0725 (7)	0.0793 (5)	8.2 (5)	13.2 (7)	8.9 (5)	0.0 (5)	−2.0 (4)	1.7 (5)
C(4)	0.4390 (8)	0.1886 (4)	0.3492 (3)	8.7 (4)	3.9 (3)	4.5 (2)	0.7 (3)	1.8 (3)	0.6 (2)
C(5)	0.4149 (11)	0.2534 (4)	0.4092 (4)	19.8 (6)	5.0 (3)	6.5 (3)	5.4 (3)	5.6 (4)	1.0 (3)
C(6)	0.3246 (15)	0.3216 (8)	0.3818 (6)	22.2 (9)	16.3 (8)	8.8 (5)	7.5 (7)	2.9 (6)	−3.9 (5)
C(7)	0.7886 (7)	0.0955 (4)	0.3193 (4)	5.2 (3)	6.5 (3)	6.9 (4)	−1.0 (3)	−0.6 (3)	0.7 (3)
C(8)	0.9591 (10)	0.1054 (7)	0.3556 (5)	8.5 (5)	16.5 (8)	9.5 (5)	−0.8 (5)	−4.4 (4)	4.5 (5)
C(9)	0.9972 (11)	0.0864 (7)	0.4265 (6)	9.9 (6)	14.3 (7)	9.6 (5)	−1.0 (6)	1.1 (5)	−2.0 (6)
C(10)	0.5731 (7)	−0.0365 (4)	0.1624 (3)	6.3 (3)	4.1 (3)	5.2 (3)	0.4 (2)	1.4 (2)	−0.3 (2)
C(11)	0.6006 (10)	−0.1051 (6)	0.1101 (4)	13.5 (5)	10.0 (5)	6.4 (3)	−0.5 (4)	5.3 (3)	−2.0 (4)
C(12)	0.6692 (15)	−0.0840 (7)	0.0600 (7)	19 (1)	10.8 (7)	19 (1)	−2.6 (7)	4.3 (9)	−5.9 (7)
C(13)	0.6349 (9)	0.3383 (5)	0.1739 (4)	10.0 (4)	5.7 (3)	7.6 (4)	−2.6 (3)	2.6 (3)	−0.9 (3)
C(14)	0.6931 (7)	0.2142 (5)	0.0773 (4)	6.8 (3)	7.5 (4)	8.3 (3)	0.2 (3)	4.4 (2)	0.2 (3)
C(15)	0.3221 (7)	−0.0630 (4)	0.4399 (4)	6.2 (3)	6.2 (3)	7.2 (3)	0.6 (3)	2.9 (2)	−0.6 (3)
C(16)	0.3616 (8)	−0.1798 (4)	0.3326 (4)	10.6 (4)	4.8 (3)	6.4 (3)	−2.1 (3)	3.0 (3)	−0.7 (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 $Rh_2(O_2CCF_3)_4(Me_2SO)_2$ (2)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	0.06851 (3)	−0.00114 (3)	0.14642 (3)	2.15 (1)	2.55 (1)	1.72 (1)	−0.02 (1)	0.416 (9)	0.740 (9)
S	0.2626 (2)	0.1061 (1)	0.6007 (1)	5.13 (6)	3.99 (5)	2.01 (3)	−1.09 (5)	0.16 (4)	1.23 (3)
F(1)	0.3646 (5)	0.4694 (4)	0.3233 (5)	5.7 (2)	4.6 (1)	6.1 (2)	−2.2 (1)	−1.2 (1)	2.0 (1)
F(2)	0.2533 (6)	0.4746 (4)	0.0716 (5)	12.5 (2)	5.5 (1)	5.1 (1)	−4.2 (1)	1.6 (1)	1.9 (1)
F(3)	0.1222 (6)	0.5300 (5)	0.2472 (8)	8.1 (2)	3.8 (2)	17.0 (4)	1.8 (2)	6.0 (2)	1.5 (2)
F(4)	0.4811 (5)	0.1771 (7)	0.0351 (7)	3.7 (1)	13.4 (3)	7.6 (2)	2.2 (2)	1.6 (1)	0.7 (2)
F(5)	0.3831 (6)	0.7888 (7)	0.7133 (6)	11.4 (2)	16.1 (3)	10.2 (2)	8.4 (2)	8.6 (1)	7.5 (2)
F(6)	0.3330 (6)	0.6369 (5)	0.8093 (8)	12.4 (2)	4.3 (2)	26.7 (4)	3.1 (2)	13.5 (2)	3.3 (2)
O(1)	0.0563 (4)	0.2135 (3)	0.9523 (4)	3.4 (1)	2.9 (1)	2.31 (9)	−0.3 (1)	0.57 (8)	0.90 (8)
O(2)	0.1827 (4)	0.2106 (3)	0.2246 (4)	2.7 (1)	3.4 (1)	2.5 (1)	−0.4 (1)	0.39 (8)	1.00 (8)
O(3)	0.1252 (4)	0.9022 (4)	0.7949 (4)	3.0 (1)	3.7 (1)	2.6 (1)	0.3 (1)	1.01 (8)	1.13 (8)
O(4)	0.2532 (4)	0.8982 (4)	0.0658 (4)	3.1 (1)	3.6 (1)	2.6 (1)	0.8 (1)	0.67 (9)	1.02 (9)
O(5)	0.1912 (4)	0.9839 (4)	0.4109 (4)	4.4 (2)	3.1 (1)	2.4 (1)	−0.1 (1)	0.3 (1)	0.96 (8)
C(1)	0.1471 (5)	0.2710 (5)	0.1124 (5)	2.6 (2)	2.9 (1)	2.6 (1)	0.2 (1)	0.7 (1)	1.0 (1)
C(2)	0.2221 (7)	0.4385 (6)	0.1893 (7)	4.1 (2)	2.7 (2)	3.4 (2)	−0.3 (2)	0.9 (1)	0.9 (1)
C(3)	0.2356 (5)	0.8693 (5)	0.9087 (6)	2.4 (2)	2.8 (2)	2.8 (1)	−0.1 (1)	0.6 (1)	0.7 (1)
C(4)	0.3667 (6)	0.7746 (6)	0.8461 (7)	3.5 (2)	4.2 (2)	3.9 (2)	1.0 (2)	1.8 (1)	1.1 (2)
C(5)	0.1251 (8)	0.2505 (7)	0.6107 (7)	5.7 (2)	4.8 (3)	3.7 (2)	0.1 (2)	2.2 (2)	0.5 (2)
C(6)	0.4430 (8)	0.2145 (7)	0.6174 (8)	4.0 (2)	6.0 (3)	4.6 (2)	−1.6 (2)	−0.0 (2)	1.9 (2)

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

Figure 1 and Table II, the thermal parameters for the propionate carbon atoms are relatively large. This results in an artificial shortening of terminal–penultimate carbon distances to an average of 1.344 (11) Å compared to an average carboxylate carbon–penultimate carbon distance of 1.520 (8) Å. In the coordinated Me_2SO molecules, average S–O and S–C bond lengths and O–S–C and C–S–C angles are 1.477 (4) Å, 1.795 (6) Å, 108.9 (3)°, and 99.8 (3)°, respectively.

$Rh_2(O_2CCF_3)_4(Me_2SO)_2$, 2. One formula unit of **2** is found in the unit cell. The molecule is located about a crystallographic center of inversion with the inversion center at the midpoint of the Rh–Rh bond. Figure 2 displays the molecular unit which shows that Me_2SO molecules coordinate through their oxygen atoms and occupy the axial positions. The Rh–Rh bond length is 2.419 (1) Å, and the Rh–O(5) distance is 2.236 (3) Å. The Rh′–Rh–O(5) linkage is nearly linear with an angle about Rh of 177.09 (7)°. The Rh atom lies 0.08 Å out of the carboxylate–oxygen atom plane toward O(5). The Me_2SO molecule has a S–O(5) bond length of 1.525 (3) Å and an average S–C distance of 1.802 (3) Å. The O–S–C angle averages 106.4 (2)° while the C(5)–S–C(6) angle is 98.5 (3)°.

Infrared Spectra. The infrared spectra of both compounds were examined as mineral oil mulls. For **1** there is an extremely strong band at 1095 ± 5 cm^{-1} that can be assigned as ν_{SO}. This is very similar to the observation[2] of ν_{SO} at 1086 cm^{-1} (which we have confirmed) in $Rh_2(O_2CCH_3)_4(Me_2SO)_2$. The validity of the infrared criterion[4] for S-bonded Me_2SO is again confirmed. For compound **2** there is *no* infrared band between 1030 and 1150 cm^{-1}, but there is a doublet of medium to high intensity at 943 (m) and 939 (s) cm^{-1} which is indicative of O-bonded Me_2SO.

Table IV. Bond Distances (Å) and Angles (Deg) for $Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$ (1)

Distances

Rh(1)-Rh(2)	2.407 (1)	O(1)-C(1)	1.309 (6)
Rh(1)-S(1)	2.453 (1)	O(2)-C(1)	1.240 (6)
Rh(1)-O(1)	2.025 (3)	O(3)-C(4)	1.259 (6)
Rh(1)-O(3)	2.026 (3)	O(4)-C(4)	1.229 (6)
Rh(1)-O(5)	2.028 (3)	O(5)-C(7)	1.255 (6)
Rh(1)-O(7)	2.027 (3)	O(6)-C(7)	1.280 (6)
Rh(2)-S(2)	2.445 (1)	O(7)-C(10)	1.251 (6)
Rh(2)-O(2)	2.025 (3)	O(8)-C(10)	1.279 (6)
Rh(2)-O(4)	2.033 (3)	C(1)-C(2)	1.493 (7)
Rh(2)-O(6)	2.019 (4)	C(2)-C(3)	1.454 (9)
Rh(2)-O(8)	2.042 (3)	C(4)-C(5)	1.539 (8)
S(1)-O(10)	1.460 (4)	C(5)-C(6)	1.379 (11)
S(1)-C(15)	1.796 (5)	C(7)-C(8)	1.559 (9)
S(1)-C(16)	1.793 (6)	C(8)-C(9)	1.298 (11)
S(2)-O(9)	1.493 (4)	C(10)-C(11)	1.489 (8)
S(2)-C(13)	1.798 (6)	C(11)-C(12)	1.245 (12)
S(2)-C(14)	1.795 (5)		

Angles

Rh(2)-Rh(1)-S(1)	178.30 (3)	O(10)-S(1)-C(15)	108.7 (2)
Rh(2)-Rh(1)-O(1)	88.61 (9)	O(10)-S(1)-C(16)	109.2 (3)
Rh(2)-Rh(1)-O(3)	87.51 (9)	C(15)-S(1)-C(16)	100.1 (3)
Rh(2)-Rh(1)-O(5)	86.9 (1)	Rh(2)-S(2)-O(9)	120.1 (2)
Rh(2)-Rh(1)-O(7)	87.8 (1)	Rh(2)-S(2)-C(13)	110.4 (2)
S(1)-Rh(1)-O(1)	89.7 (1)	Rh(2)-S(2)-C(14)	106.7 (2)
S(1)-Rh(1)-O(3)	92.29 (9)	O(9)-S(2)-C(13)	109.9 (3)
S(1)-Rh(1)-O(5)	94.7 (1)	O(9)-S(2)-C(14)	108.0 (3)
S(1)-Rh(1)-O(7)	92.4 (1)	C(13)-S(2)-C(14)	99.6 (3)
O(1)-Rh(1)-O(3)	89.9 (2)	Rh(1)-O(1)-C(1)	118.0 (3)
O(1)-Rh(1)-O(5)	175.5 (1)	Rh(2)-O(2)-C(1)	120.9 (3)
O(1)-Rh(1)-O(7)	90.1 (1)	Rh(1)-O(3)-C(4)	119.3 (3)
O(3)-Rh(1)-O(5)	89.1 (2)	Rh(2)-O(4)-C(4)	120.0 (3)
O(3)-Rh(1)-O(7)	175.3 (1)	Rh(1)-O(5)-C(7)	120.4 (3)
O(5)-Rh(1)-O(7)	90.5 (1)	Rh(2)-O(6)-C(7)	118.4 (3)
Rh(1)-Rh(2)-S(2)	179.52 (3)	Rh(1)-O(7)-C(10)	120.5 (3)
Rh(1)-Rh(2)-O(2)	87.31 (9)	Rh(2)-O(8)-C(10)	119.5 (3)
Rh(1)-Rh(2)-O(4)	87.1 (1)	O(1)-C(1)-O(2)	125.2 (5)
Rh(1)-Rh(2)-O(6)	88.7 (1)	O(1)-C(1)-C(2)	116.5 (5)
Rh(1)-Rh(2)-O(8)	87.5 (1)	O(2)-C(1)-C(2)	118.3 (5)
S(2)-Rh(2)-O(2)	93.0 (1)	C(1)-C(2)-C(3)	113.5 (6)
S(2)-Rh(2)-O(4)	93.3 (1)	O(3)-C(4)-O(4)	126.0 (5)
S(2)-Rh(2)-O(6)	91.0 (1)	O(3)-C(4)-C(5)	115.3 (5)
S(2)-Rh(2)-O(8)	92.1 (1)	O(4)-C(4)-C(5)	118.5 (5)
O(2)-Rh(2)-O(4)	89.7 (1)	C(4)-C(5)-C(6)	114.7 (6)
O(2)-Rh(2)-O(6)	175.9 (1)	O(5)-C(7)-O(6)	125.5 (5)
O(2)-Rh(2)-O(8)	90.5 (1)	O(5)-C(7)-C(8)	118.0 (5)
O(4)-Rh(2)-O(6)	89.3 (1)	O(6)-C(7)-C(8)	116.3 (6)
O(4)-Rh(2)-O(8)	174.6 (1)	C(7)-C(8)-C(9)	116.0 (9)
O(6)-Rh(2)-O(8)	90.2 (1)	O(7)-C(10)-O(8)	124.6 (5)
Rh(1)-S(1)-O(10)	118.7 (2)	O(7)-C(10)-O(11)	114.7 (5)
Rh(1)-S(1)-C(15)	110.0 (2)	O(8)-C(10)-C(11)	120.7 (5)
Rh(1)-S(1)-C(16)	108.4 (2)	C(10)-C(11)-C(12)	116.5 (9)

Discussion

The results of this study are of interest from two vantage points: that of the electronic structure and Lewis acidity of the $Rh_2(O_2CR)_4$ unit and that of the ligand properties of Me_2SO. We shall discuss them in that order.

We have here a unique example of control of the mode of coordination of the ambidentate sulfoxide ligand solely by changing the other ligands that are bound to the metal atom, without changing the identity or oxidation number of the metal atom. This control is effected by a pure inductive influence, with the more electron-donating substituents (CH_3, C_2H_5) causing the metal atom to prefer the sulfur atom and the strongly electron-withdrawing substituent (CF_3) changing the preference in favor of the oxygen atom. This effect is, of course, consistent with the well-known tendency, referred to in the Introduction, of *different* metal atoms to prefer S or O. It is well-known that the least polarizable (usually smaller and/or more highly charged) metal ions prefer O bonding while the more polarizable (usually larger and/or less charged) metal ions prefer S bonding. It is unexpected that the same metal ion can have its preference changed simply by changing the effective electronegativity of groups removed by three bonds from the metal atom. The interesting question is raised as to whether this sensitivity is due to some feature of the electron configuration of the Rh_2^{4+} unit that it shares with other dimetal units, such as Cr_2^{4+} or Re_2^{6+}. The Rh_2^{4+} unit differs from these others in having filled π^* and δ^* orbitals as well as the quadruply bonding $\sigma^2\pi^4\delta^2$ configuration,[12] and

Table V. Bond Distances (Å) and Angles (Deg) for $Rh_2(O_2CCF_3)_4(Me_2SO)_2$ (2)

Distances

Rh-Rh′	2.419 (1)	F(3)-C(2)	1.293 (5)
Rh-O(1)′	2.031 (3)	F(4)-C(4)	1.310 (6)
Rh-O(2)	2.022 (3)	F(5)-C(4)	1.279 (6)
Rh-O(3)′	2.016 (3)	F(6)-C(4)	1.239 (6)
Rh-O(4)	2.029 (3)	O(1)-C(1)	1.239 (5)
Rh-O(5)	2.236 (3)	O(2)-C(1)	1.263 (5)
S-O(5)	1.525 (3)	O(3)-C(3)	1.239 (5)
S-C(5)	1.776 (5)	O(4)-C(3)	1.248 (5)
S-C(6)	1.829 (5)	C(1)-C(2)	1.530 (5)
F(1)-C(2)	1.305 (6)	C(3)-C(4)	1.541 (5)
F(2)-C(2)	1.317 (6)		

Angles

Rh′-Rh-O(1)′	87.77 (8)	Rh-O(4)-C(3)	117.0 (3)
Rh′-Rh-O(2)	87.48 (8)	Rh-O(5)-S	132.4 (2)
Rh′-Rh-O(3)′	87.21 (8)	O(1)-C(1)-O(2)	128.2 (4)
Rh′-Rh-O(4)	87.89 (8)	O(1)-C(1)-C(2)	117.2 (3)
Rh′-Rh-O(5)	177.09 (7)	O(2)-C(1)-C(2)	114.5 (3)
O(1)′-Rh-O(2)	175.24 (9)	F(1)-C(2)-F(2)	105.5 (4)
O(1)′-Rh-O(3)′	90.8 (1)	F(1)-C(2)-F(3)	106.8 (4)
O(1)′-Rh-O(4)	88.7 (1)	F(1)-C(2)-C(1)	112.6 (4)
O(1)′-Rh-O(5)	89.4 (1)	F(2)-C(2)-F(3)	108.7 (4)
O(2)-Rh-O(3′)	88.8 (1)	F(2)-C(2)-C(1)	112.4 (3)
O(2)-Rh-O(4)	91.3 (1)	F(3)-C(2)-C(1)	110.4 (4)
O(2)-Rh-O(5)	95.3 (1)	O(3)-C(3)-O(4)	129.2 (4)
O(3)′-Rh-O(4)	175.1 (1)	O(3)-C(3)-C(4)	115.7 (3)
O(3)′-Rh-O(5)	93.6 (1)	O(4)-C(3)-C(4)	115.1 (3)
O(4)-Rh-O(5)	91.3 (1)	F(4)-C(4)-F(5)	100.6 (5)
O(5)-S-C(5)	106.2 (2)	F(4)-C(4)-F(6)	109.7 (5)
O(5)-S-C(6)	106.7 (2)	F(4)-C(4)-C(3)	112.4 (4)
C(5)-S-C(6)	98.5 (3)	F(5)-C(4)-F(6)	109.4 (5)
Rh-O(1)′-C(1)′	118.0 (2)	F(5)-C(4)-C(3)	114.0 (4)
Rh-O(2)-C(1)	118.3 (2)	F(6)-C(4)-C(3)	110.4 (4)
Rh-O(3)′-C(3)′	118.6 (3)		

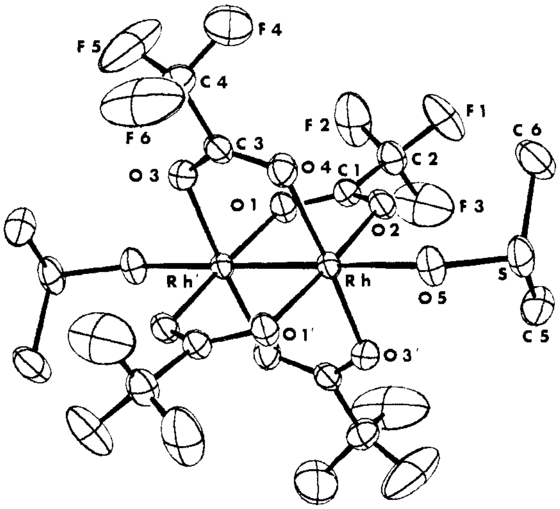

Figure 2. ORTEP drawing of $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, **2**, with vibrational ellipsoids scaled so as to enclose 40% of their electron density. A crystallographic center of inversion is located at the midpoint of the Rh–Rh bond.

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[12] Norman, J. G., Jr.; Renzoni, G. E.; Case, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5256.

Table VI. Structural and Infrared Data for $Rh_2(O_2CR)_4(Me_2SO)_2$ Compounds

R	Rh-Rh, Å	Rh-X, Å	S-O, Å	ν_{SO},[a] cm^{-1}
CH_3	2.406 (1)	2.451 (1)[b]	1.477 (5)	1085
C_2H_5	2.407 (1)	2.449 (1)[b,c]	1.477 (4)[c]	1095
CF_3	2.419 (1)	2.236 (3)[d]	1.525 (3)	939, 943

[a] Samples run as Nujol mulls. [b] X = axial ligand = $S(Me_2SO)$. [c] Average value. [d] X = axial ligand = $O(Me_2SO)$.

it may be these rather loosely held antibonding electrons that are most important.

The replacement of alkyl by CF_3 groups in the $Rh_2(O_2CR)_4$ molecule has already been shown to cause a general increase in its Lewis acidity. Drago and co-workers,[13] in a study of nitroxide spin-label adducts, observed that only $Rh_2(O_2CCF_3)_4$ (and not the analogous $Rh_2(O_2CC_3H_7)_4$ compound) forms a stable 1:1 adduct. Bear and co-workers[14] noted also the profound effect of the highly electronegative CF_3 substituents on stabilizing the lower oxidation states of Rh. In their electrochemical investigation, Bear et al.[14] found that no oxidation of $Rh_2(O_2CCF_3)_4$ occurs up to the potential limit of the solvent, whereas reduction of this compound is favored by 500 mV over $Rh_2(O_2CCH_3)_4$.

The Rh–Rh bond length in **1** of 2.407 (1) Å is in accord with our previous work[1] involving axially bound sulfur-donor ligands. The electronegative oxygen atom on the S-bonded Me_2SO enhances the Rh to S π back-bonding which makes the sulfoxide ligand slightly more effective in bonding to the rhodium (Rh–S = 2.449 (1) Å, average) than an alkyl sulfur ligand like tetrahydrothiophene (THT) which in $Rh_2(O_2CCH_3)_4(THT)_2$ has a Rh–S bond length of 2.517 (1) Å. The effect of the Me_2SO and THT ligands on the Rh–Rh bond length is essentially the same with the THT complex (Rh–Rh = 2.413 (1) Å), showing, somewhat surprisingly, a marginally longer bond length. However, phosphine and phosphite ligands in $Rh_2(O_2CR)_4L_2$ compounds provide the greatest effect thus far observed on the Rh–Rh bond. The combined σ-donating and π-accepting ability of phosphorus donor ligands has led to Rh–Rh distances in the range 2.43–2.45 Å for $Rh_2(O_2CR)_4L_2$ compounds.[15]

The bond lengths and ν_{SO} frequencies in the sulfoxide ligands (Table VI) vary as expected with the mode of bonding. For both compounds with S-bonded Me_2SO the S–O bond lengths are the same, 1.477 Å, while that in the O-bonded case, 1.525 Å, is 0.048 Å greater. This difference is highly significant, being an order of magnitude greater than the level of the esd's (ca. 0.004 Å) in the individual distances. The difference in the ν_{SO} frequencies for the two S-bonded compounds is not significant in view of the estimated uncertainties; a frequency of 1090 ± 5 cm^{-1} may be attributed to both. The difference between this frequency and those for O-bonded Me_2SO, ca. 150 cm^{-1}, is consistent with those previously observed when the mode of bonding was changed by changing the identity of the metal atom.[3,4]

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Registry No. 1, 65507-56-4; **2**, 72665-42-0; $Rh_2(O_2CC_2H_5)_4(H_2O)_2$, 60801-05-0; $Rh_2(O_2CCF_3)_4$, 31126-95-1.

Supplementary Material Available: Tables of observed and calculated structure factors (23 pages) for both compounds. Ordering information is given on any current masthead page.

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