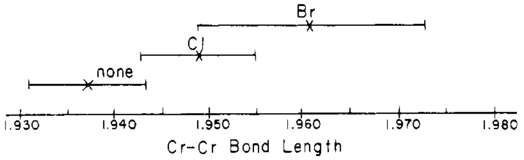

Figure 3. Plot of the Cr–Cr bond length showing the 3σ error limit, in the compounds $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4\cdot 1.5C_6H_5CH_3$ and $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4\cdot 2CH_2X_2$, X = Cl, Br.

The question of why the Cr–Cr bond is ca. 0.07 Å longer in $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4$ than in $Cr_2[PhNC(CH_3)O]_4$, which we shall henceforth refer to simply as the xylyl and the phenyl compounds, is one we cannot unequivocally answer. This appreciable difference was not, as already emphasized, an expected result. Since our attempt to explain the observation will be rather speculative, it will, in accord with the "First Law of Well-Regulated Discourse"[11] be kept brief.

We do not believe that the simple inductive effect of replacing hydrogen atoms at the 2- and 6-positions can account for the results. We turn instead to the indirect effect of these methyl groups, namely, their influence on the dihedral angle between the phenyl or xylyl group and the plane of the bridging amido group. As we have reported above, in the phenyl compound this angle is 48° (cos 48° = 0.67) while in the xylyl compound steric factors require it to be essentially 90° (cos 90° = 0). This means that in the phenyl compound conjugation of the phenyl π system with the amide π system is about two-thirds the maximum possible value while in the xylyl compound conjugation is shut off completely. Our tentative explanation of the change in Cr–Cr bond length would then be as follows. Delocalization of phenyl π-electron density toward the Cr_2^{4+} unit reduces its positive charge thus allowing slight expansion of the 3d orbitals and increasing their overlap in the σ, π, and/or δ components of the quadruple bond. This bond, is, therefore, stronger and shorter in the phenyl compound, where considerable conjugation is possible than in the xylyl compound where no conjugation can occur.

A test of this proposal would require the synthesis of Cr_2L_4 compounds containing ligands, L, which permit even smaller dihedral angles; in such compounds, the Cr–Cr distance should be even shorter than in the acetanilido compound. Efforts to prepare and structurally characterize one or more such compounds will be made.

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Registry No. **1**, 77611-46-2; **2**, 77611-47-3; **3**, 77611-48-4; $Cr_2(O_2CCH_3)_4$, 15020-15-2; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Listings of observed and calculated structure factors for all three structures (25 pages). Ordering information is given on any current mashead page.

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Crystal and Molecular Structure of Tetrakis(trifluoroacetato)bis(dimethyl sulfone)dirhodium(II). A Compound with Axially Coordinated Sulfone Ligands

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Dark green crystals of the title compound are deposited upon slow evaporaton of a benzene–chloroform solution of $Rh_2(O_2CCF_3)_4$ containing excess dimethyl sulfone. The crystals belong to the triclinic space group $P\bar{1}$ with two molecules in a unit cell of dimensions $a = 10.482$ (1) Å, $b = 14.004$ (2) Å, $c = 9.533$ (2) Å, $\alpha = 108.17$ (2)°, $\beta = 101.64$ (2)°, $\gamma = 82.27$ (1)°, and $V = 1298.3$ (8) Å^3. The structure was solved with use of a combination of Patterson and direct methods to locate the two independent Rh atoms followed by full-matrix least-squares refinement and difference Fourier techniques. A total of 3682 independent reflections (Mo K$\bar{\alpha}$) with $I > 3\sigma(I)$ were used to refine the 40 nonhydrogen atoms to final discrepancy indices of $R_1 = 0.048$ and $R_2 = 0.068$. Two crystallographically unique $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$ molecules (A and B) are found in the unit cell on centers of inversion with Rh–Rh bond lengths of 2.401 (1) and 2.399 (1) Å for molecules A and B, respectively. The four trifluoroacetate groups bridge the Rh–Rh bonds with the axial positions occupied by dimethyl sulfone molecules which coordinate to the Rh atoms through one of their two oxygen atoms at distances of 2.291 (3) and 2.284 (3) Å. Bond distances and angles within the two independent molecules in the crystallographic asymmetric unit are essentially identical. The coordinated dimethyl sulfone molecules exhibit a distorted tetrahedral geometry about the sulfur atoms with average S–O bond lengths which are essentially the same for both the coordinated (1.455 (3) Å) and uncoordinated (1.450 (4) Å) sulfone oxygen atoms.

Introduction

Much current work on metal–metal bonded compounds is concerned with understanding the interaction of axial ligands with the dimetal unit and the resulting effect upon the metal–metal bond length. Quadruply bonded dichromium(II) compounds display an unusual sensitivity in the Cr–Cr bond length toward coordination by ligands along the Cr–Cr bond axis.[1,2] A considerable number of axial ligands have been used although they have been largely limited to relatively weak σ-donor ligands having nitrogen, oxygen, or halogen donor atoms.[1-4] Such a variety of adducts is not currently known

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Table I. 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(1)	0.96213 (4)	0.08079 (3)	0.07540 (5)	2.10 (2)	1.90 (2)	2.79 (2)	0.05 (1)	0.61 (1)	0.25 (1)
Rh(2)	0.46190 (4)	0.42207 (3)	0.41547 (5)	1.94 (2)	2.01 (2)	3.25 (2)	−0.15 (1)	0.28 (2)	0.07 (1)
S(10)	0.9512 (2)	0.3291 (1)	0.2982 (2)	2.79 (6)	2.55 (6)	4.34 (7)	−0.15 (5)	0.91 (5)	−0.19 (6)
S(20)	0.4539 (2)	0.1814 (1)	0.1653 (2)	2.64 (6)	2.57 (6)	4.33 (7)	−0.23 (5)	0.68 (6)	−0.18 (6)
F(1)	1.2892 (4)	0.0976 (3)	−0.2559 (5)	4.8 (2)	5.6 (2)	6.9 (2)	0.4 (2)	3.1 (1)	2.7 (1)
F(2)	1.1898 (6)	0.2333 (3)	−0.1523 (7)	15.1 (3)	3.3 (2)	15.8 (3)	0.2 (2)	11.1 (2)	2.7 (2)
F(3)	1.0967 (7)	0.1297 (5)	−0.3532 (6)	6.9 (3)	16.2 (3)	10.4 (2)	0.8 (3)	1.0 (2)	10.6 (2)
F(4)	1.3411 (5)	0.0760 (4)	0.4238 (5)	5.5 (2)	6.6 (2)	4.6 (2)	−0.4 (2)	−1.3 (2)	−0.3 (2)
F(5)	1.2673 (7)	−0.0588 (4)	0.4168 (6)	10.0 (4)	8.8 (3)	6.0 (2)	−1.3 (3)	−1.2 (2)	4.4 (2)
F(6)	1.4164 (5)	−0.0619 (5)	0.2884 (6)	5.0 (2)	9.4 (3)	5.7 (3)	3.5 (2)	−1.1 (2)	0.1 (2)
F(7)	0.1528 (5)	0.7414 (3)	0.4112 (6)	5.5 (2)	4.6 (2)	7.9 (3)	2.0 (2)	−0.1 (2)	1.6 (2)
F(8)	0.2320 (7)	0.6846 (5)	0.2139 (6)	10.5 (4)	10.2 (3)	6.5 (2)	2.7 (3)	1.4 (3)	4.5 (2)
F(9)	0.0846 (6)	0.6083 (4)	0.2550 (8)	5.4 (2)	5.2 (2)	15.8 (4)	−0.7 (2)	−5.4 (3)	3.0 (3)
F(10)	0.7839 (5)	0.5817 (4)	0.2230 (5)	5.4 (2)	7.2 (2)	5.6 (2)	−3.0 (2)	1.1 (2)	1.6 (2)
F(11)	0.6923 (6)	0.4553 (4)	0.0686 (5)	9.7 (3)	8.4 (3)	4.7 (2)	−4.0 (2)	3.3 (2)	−1.2 (2)
F(12)	0.5883 (7)	0.6006 (4)	0.1157 (6)	8.1 (4)	12.0 (3)	9.0 (2)	0.7 (3)	0.1 (3)	7.6 (2)
O(1)	1.0591 (4)	0.1439 (3)	−0.0330 (5)	3.3 (2)	2.2 (1)	4.8 (2)	0.2 (1)	1.6 (1)	0.8 (1)
O(2)	1.1223 (4)	0.0720 (3)	0.2308 (5)	2.9 (2)	3.1 (2)	3.1 (2)	0.1 (2)	0.4 (2)	−0.1 (1)
O(3)	1.1312 (4)	−0.0076 (3)	−0.1747 (5)	3.3 (2)	2.7 (2)	4.0 (2)	0.2 (1)	1.5 (1)	0.8 (1)
O(4)	1.1955 (4)	−0.0795 (3)	0.0887 (5)	2.3 (2)	2.8 (2)	3.7 (2)	0.6 (1)	0.4 (1)	0.4 (1)
O(5)	0.3028 (4)	0.5021 (3)	0.3347 (5)	2.4 (2)	2.8 (2)	4.2 (2)	−0.1 (1)	−0.2 (2)	0.2 (2)
O(6)	0.5577 (4)	0.4427 (3)	0.2626 (5)	3.1 (2)	3.3 (2)	3.6 (2)	−0.6 (2)	0.7 (1)	0.1 (1)
O(7)	0.3768 (4)	0.6484 (3)	0.4924 (5)	2.7 (2)	2.7 (2)	4.4 (2)	0.1 (1)	0.1 (2)	0.3 (2)
O(8)	0.6300 (4)	0.5891 (3)	0.4226 (5)	2.9 (2)	2.9 (2)	4.0 (2)	−0.6 (1)	0.6 (1)	0.4 (1)
O(10)	0.8908 (4)	0.2354 (3)	0.2190 (5)	2.7 (2)	3.0 (2)	4.5 (2)	−0.3 (1)	0.9 (2)	−0.2 (2)
O(11)	0.8682 (5)	0.4093 (3)	0.3811 (6)	4.8 (2)	2.7 (2)	4.8 (2)	0.6 (2)	0.8 (2)	−0.3 (2)
O(20)	0.3914 (4)	0.2725 (3)	0.2564 (5)	2.8 (2)	2.8 (2)	4.5 (2)	−0.2 (1)	0.8 (2)	−0.1 (2)
O(21)	0.3695 (5)	0.1004 (3)	0.0864 (6)	4.7 (2)	2.6 (2)	4.3 (2)	−0.3 (2)	0.1 (2)	−0.3 (2)
C(1)	1.1177 (6)	0.0862 (5)	−0.1342 (7)	2.8 (2)	3.0 (2)	4.0 (3)	0.0 (2)	1.1 (2)	1.1 (2)
C(2)	1.1754 (8)	0.1377 (5)	−0.2242 (9)	5.3 (3)	4.2 (3)	7.1 (3)	1.3 (3)	2.9 (3)	3.4 (2)
C(3)	1.2002 (6)	−0.0054 (5)	0.2037 (7)	2.7 (2)	2.8 (2)	3.3 (2)	0.2 (2)	0.4 (2)	1.0 (2)
C(4)	1.3088 (8)	−0.0137 (6)	0.3361 (8)	4.4 (4)	5.0 (3)	3.4 (3)	0.9 (3)	−0.2 (3)	0.6 (3)
C(5)	0.2992 (6)	0.5956 (5)	0.3889 (7)	2.6 (2)	3.1 (3)	3.6 (3)	0.2 (2)	0.3 (2)	0.3 (2)
C(6)	0.1888 (8)	0.6577 (5)	0.3149 (9)	4.1 (3)	3.6 (3)	5.1 (3)	0.1 (3)	−0.8 (3)	1.1 (3)
C(7)	0.6161 (6)	0.5218 (5)	0.3001 (7)	2.7 (2)	3.4 (3)	3.8 (3)	−0.3 (2)	0.4 (2)	1.1 (2)
C(8)	0.6726 (9)	0.5401 (6)	0.1737 (8)	5.3 (4)	6.0 (4)	4.0 (3)	−1.4 (3)	0.5 (3)	1.7 (2)
C(10)	1.0107 (10)	0.3700 (6)	0.1671 (10)	8.0 (4)	3.9 (3)	8.5 (4)	−0.8 (3)	4.6 (3)	1.3 (3)
C(11)	1.0940 (9)	0.3060 (8)	0.4209 (11)	3.8 (4)	6.7 (5)	5.9 (5)	0.2 (4)	−0.9 (4)	−0.4 (4)
C(20)	0.5259 (10)	0.2163 (7)	0.0382 (10)	8.2 (4)	6.6 (4)	6.7 (4)	−2.5 (4)	4.4 (3)	−0.4 (3)
C(21)	0.5879 (9)	0.1360 (6)	0.2768 (13)	4.4 (4)	3.9 (3)	9.6 (6)	0.4 (3)	−1.9 (4)	1.0 (4)

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

for dimetal complexes of Mo_2^{4+},[5] Tc_2^{5+},[6] Ru_2^{5+},[7] Re_2^{6+},[8] and Os_2^{6+}.[9] On the other hand, adducts of Rh_2^{4+}, particularly those of the type $Rh_2(O_2CR)_4L_2$, have shown a much greater range in the σ- and π-donor characteristics of the axial ligand, L.[10-14] In the dirhodium(II) carboxylates, it has been shown that a change in the carboxylate R group can profoundly alter the preference of the rhodium atoms toward different types of axial donor atoms. For example, when R = CH_3 or C_2H_5, dimethyl sulfoxide (Me_2SO) is found to coordinate through the sulfur atom.[13,15] However, when R = CF_3, axial coordination of Me_2SO occurs through the oxygen atom.[15]

Since the first report[16] on the rhodium(II) trifluoroacetate dimer in 1963, several other studies have appeared on its preparation, adduct formation, and physical properties.[15,17-23] The dimer exhibits catalytic activity toward the cyclopropanation of alkenes with alkyl diazoacetates,[24] although it is not as effective as the corresponding butyrate and pivalate complexes, and catalyzes the oxidation of cyclohexene in the presence of a vanadium catalyst.[25] Preferential binding of a weakly basic nitroxide ligand to dirhodium(II) trifluoroacetate over the corresponding butyrate complex[22] suggests that the electron-withdrawing trifluoroacetate groups enhance the Lewis acidity of the Rh atoms so as to allow coordination by weakly donating ligands such as nitroxide. Accordingly, it was of interest to ascertain if other weak donor ligands, not normally known to form metal complexes, could bind to $Rh_2(O_2CCF_3)_4$.

In contrast to the relative ease with which sulfoxides have

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Table II. Bond Distances (Å) and Angles (Deg) for $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$

Distances

Rh(1)-Rh(1′)	2.401 (1)	F(3)-C(2)	1.317 (8)
-O(1)	2.029 (3)	F(4)-C(4)	1.318 (7)
-O(2)	2.021 (3)	F(5)-C(4)	1.300 (7)
-O(3′)	2.038 (3)	F(6)-C(4)	1.321 (7)
-O(4′)	2.031 (3)	F(7)-C(6)	1.307 (7)
-O(10)	2.291 (3)	F(8)-C(6)	1.311 (8)
Rh(2)-Rh(2′)	2.399 (1)	F(9)-C(6)	1.305 (7)
-O(5)	2.036 (3)	F(10)-C(8)	1.308 (7)
-O(6)	2.036 (3)	F(11)-C(8)	1.316 (7)
-O(7′)	2.024 (3)	F(12)-C(8)	1.303 (8)
-O(8′)	2.031 (3)	O(1)-C(1)	1.257 (6)
-O(20)	2.284 (3)	O(2)-C(3)	1.257 (5)
S(10)-O(10)	1.452 (3)	O(3)-C(1)	1.245 (6)
-O(11)	1.450 (4)	O(4)-C(3)	1.250 (6)
-C(10)	1.770 (6)	O(5)-C(5)	1.247 (6)
-C(11)	1.764 (6)	O(6)-C(7)	1.256 (6)
S(20)-O(20)	1.458 (3)	O(7)-C(5)	1.252 (6)
-O(21)	1.451 (4)	O(8)-C(7)	1.247 (6)
-C(20)	1.764 (7)	C(1)-C(2)	1.528 (7)
-C(21)	1.757 (6)	C(3)-C(4)	1.542 (7)
F(1)-C(2)	1.300 (7)	C(5)-C(6)	1.541 (7)
F(2)-C(2)	1.313 (8)	C(7)-C(8)	1.545 (7)

Angles

Rh(1′)-Rh(1)-O(1)	87.58 (9)	Rh(1)-O(3′)-C(1′)	117.1 (3)
-O(2)	87.67 (9)	-O(4′)-C(3′)	117.0 (3)
-O(3′)	88.33 (9)	Rh(2)-O(5)-C(5)	116.6 (3)
-O(4′)	88.37 (9)	-O(6)-C(7)	117.2 (3)
-O(10)	179.67 (8)	Rh(2)-O(7′)-C(5′)	118.1 (3)
O(1)-Rh(1)-O(2)	92.1 (1)	-O(8′)-C(7′)	117.7 (3)
-O(3′)	175.9 (1)	Rh(1)-O(10)-S(10)	134.3 (2)
-O(4′)	88.3 (1)	Rh(2)-O(20)-S(20)	134.8 (2)
-O(10)	92.1 (1)	O(1)-C(1)-O(3)	128.8 (4)
O(2)-Rh(1)-O(3′)	87.9 (1)	O(1)-C(1)-C(2)	115.7 (4)
-O(4′)	176.0 (1)	O(3)-C(1)-C(2)	115.4 (4)
-O(10)	92.2 (1)	F(1)-C(2)-F(2)	106.5 (6)
O(3′)-Rh(1)-O(4′)	91.4 (1)	-F(3)	106.5 (5)
-O(10)	92.0 (1)	-C(1)	113.9 (4)
O(4′)-Rh(1)-O(10)	91.7 (1)	F(2)-C(2)-F(3)	109.6 (5)
Rh(2′)-Rh(2)-O(5)	88.47 (9)	-C(1)	111.6 (5)
-O(6)	88.06 (9)	F(3)-C(2)-C(1)	108.6 (5)
-O(7′)	87.54 (9)	O(2)-C(3)-O(4)	128.8 (4)
-O(8′)	88.00 (9)	-C(4)	115.0 (4)
-O(20)	179.21 (9)	O(4)-C(3)-C(4)	116.0 (4)
O(5)-Rh(2)-O(6)	88.6 (1)	F(4)-C(4)-F(5)	107.5 (5)
-O(7′)	175.9 (1)	-F(6)	106.4 (5)
-O(8′)	91.0 (1)	-C(3)	111.3 (5)
-O(20)	92.3 (1)	F(5)-C(4)-F(6)	110.9 (5)
O(6)-Rh(2)-O(7′)	92.0 (1)	-C(3)	109.5 (5)
-O(8′)	176.0 (1)	F(6)-C(4)-C(3)	111.1 (4)
-O(20)	92.1 (1)	O(5)-C(5)-O(7)	129.2 (4)
O(7′)-Rh(2)-O(8′)	88.1 (1)	O(5)-C(5)-C(6)	117.1 (4)
-O(20)	91.7 (1)	O(7)-C(5)-C(6)	113.6 (4)
O(8′)-Rh(2)-O(20)	91.8 (1)	F(7)-C(6)-F(8)	106.1 (5)
O(10)-S(10)-O(11)	115.5 (2)	-F(9)	106.9 (6)
-C(10)	108.2 (3)	-C(5)	111.9 (5)
-C(11)	109.7 (3)	F(8)-C(6)-F(9)	110.6 (6)
O(11)-S(10)-C(10)	110.1 (3)	-C(5)	109.1 (5)
-C(11)	109.2 (3)	F(9)-C(6)-C(5)	112.1 (5)
C(10)-S(10)-C(11)	103.5 (4)	O(6)-C(7)-O(8)	129.0 (5)
O(20)-S(20)-O(21)	115.5 (2)	-C(8)	115.0 (4)
-C(20)	107.6 (3)	O(8)-C(7)-C(8)	116.0 (4)
-C(21)	109.8 (3)	F(10)-C(8)-F(11)	107.6 (5)
O(21)-S(20)-C(20)	110.6 (3)	-F(12)	108.6 (5)
-C(21)	109.0 (3)	-C(7)	112.3 (5)
C(20)-S(20)-C(21)	103.6 (4)	F(11)-C(8)-F(12)	109.3 (5)
Rh(1)-O(1)-C(1)	118.1 (3)	-C(7)	111.4 (5)
-O(2)-C(3)	118.1 (3)	F(12)-C(8)-C(7)	107.6 (5)

been found to coordinate to metal ions,[26,27] the corresponding sulfone complexes, as noted in work from this laboratory 20 years ago, "do not appear to form complexes with transition metals very readily, if at all..."[26] While sulfoxides may employ either the oxygen or sulfur atom for coordinating to Lewis acids, sulfones must rely solely on the oxygen lone pairs for donation. Stannic chloride has been reported[28] to form complexes of the type $SnCl_4 \cdot L$, where $L = R_2SO_2$ with $R = CH_3$, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, and C_6H_5 or L = tetramethylene sulfone ($TMSO_2$). The formulas were proposed on the basis of analytical, infrared, and Mössbauer data, but the details of the sulfone coordination are not known. The structure of $Cu_3Cl_6(H_2O)_2 \cdot 2TMSO_2$[29] consists of a trans planar trimer of $Cu_3Cl_6(H_2O)_2$ with $TMSO_2$ molecules between trimers. However, the closest copper–sulfone oxygen contact is 2.61 (1) Å which is 0.05 Å longer than that attributed to purely van der Waals forces between copper and oxygen.[29,30] While both the tin[28] and copper[29] compounds clearly involve a sulfone molecule within the complex, none of these compounds supply a proven example of a *coordinated* sulfone.

We wish to report in this paper that the interaction of $Rh_2(O_2CCF_3)_4$ with dimethyl sulfone (Me_2SO_2) in noncoordinating solvents affords the blue-green crystalline complex $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$, in which the structure as determined by X-ray crystallography contains Me_2SO_2 molecules which are axially coordinated. This may be (and to our knowledge is) the first structurally confirmed case of a complex containing a sulfone ligand.

Experimental Section

Compound Preparation. Rhodium(II) trifluoroacetate was prepared by the method of Kitchens and Bear.[19] The anhydrous compound was obtained by heating at 150 °C for 30 min.

$Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$ was prepared directly in crystalline form by dissolving $Rh_2(O_2CCF_3)_4$ in a 1:1 solution of benzene–chloroform and adding Me_2SO_2 (Aldrich) in excess. The blue-green solution upon evaporation yielded dark green crystals, mostly in the form of long, thin needles, but a few irregularly shaped prisms were also obtained. The excess Me_2SO_2 was removed by successive washing of the crystalline product with small amounts of benzene. Upon crushing, the crystals give a blue-green powder.

X-ray Crystallography. Collection of Data. A dark green prismatic crystal of dimensions 0.22 × 0.30 × 0.35 mm was selected for preliminary examination on an Enraf-Nonius CAD-4 diffractometer using a random automatic search routine. Twenty-five reflections with $22 < 2\theta < 33°$ were subsequently collected and centered. A ω-scan profile of several representative reflections showed the crystal to be of satisfactory quality. An indexing routine produced a triclinic reduced cell which did not transform to a cell of higher symmetry upon application of a Delaunay reduction. The final cell constants were obtained from 21 reflections with $25° < 2\theta < 32°$.

Crystal data: $Rh_2S_2F_{12}O_{12}C_{12}H_{12}$; mol wt 846.14; triclinic; a = 10.482 (1), b = 14.004 (2), c = 9.533 (2) Å; α = 108.17 (2), β = 101.64 (2), γ = 82.27 (1)°; V = 1298.3 (8) Å^3; Z = 2; d_c = 2.16 g/cm^3; $F(000)$ = 820; μ(Mo Kα) = 15.396 cm^{-1}; space group $P\bar{1}$.

Intensity data were collected on a CAD-4 diffractometer (Mo K$\bar{\alpha}$ radiation, $\lambda_{\bar{\alpha}}$ = 0.710 73 Å) equipped with a graphite-crystal monochromator and using an ω–2θ scan technique. The scan width ($\Delta\omega$) was $(0.70 + 0.35 \tan \theta)°$, and the aperature width was $(1.5 + \tan \theta)$ mm. The crystal-to-counter separation was 173 mm. Scans were made with a prescan rejection limit of 2.0 (0.5σ), a prescan acceptance limit of 0.02 (50σ), and a maximum scan speed of 20.12° min^{-1}. The maximum counting time for any reflection was 30 s. A total of 4536 unique data were collected for $+h$, $\pm k$, $\pm l$ reflections up to a maximum 2θ value of 50°. Three reflections were automatically monitored every 100 reflections as a check on the crystal alignment, and three additional reflections were also checked each hour of X-ray exposure time up to a total of 36 h needed to collect the data. No decomposition was noted during the data collection.

The formulas used for deriving the intensity and its standard deviation have been given previously.[31] The data were corrected for

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Table IV. Geometries of Representative Organic Sulfone Compounds[a]

compd	S-O, Å	S-C, Å	O-S-O, deg	O-S-C, deg	C-S-C, deg	ref
Me_2SO_2	1.446 (3)	1.765 (5)	117.3 (2)	108.5 (1)	104.8 (2)	35
Me_2SO_2[b]	1.425 (3)	1.770 (3)	127.1 (24)	106.2 (11)	102.5 (13)	36
$Cu_3Cl_6(H_2O)_2(TMSO_2)_2$	1.462 (11)	1.779 (15)	114.7 (7)	110.9 (8)	97.2 (8)	29
$(C_6H_5SO_2)_2N^-Na^+$	1.446 (5)	1.773 (6)	115.3 (3)	106.5 (3)	108.0 (3)[c]	34
$Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$	1.453 (4)	1.764 (4)	115.5 (2)	109.3 (3)	103.5 (4)	this work

[a] Distances and angles are mean values among chemically equivalent sets of atoms. [b] Measured by gas-phase electron diffraction. [c] This angle is for C-S-N; there is no C-S-C angle in this compound.

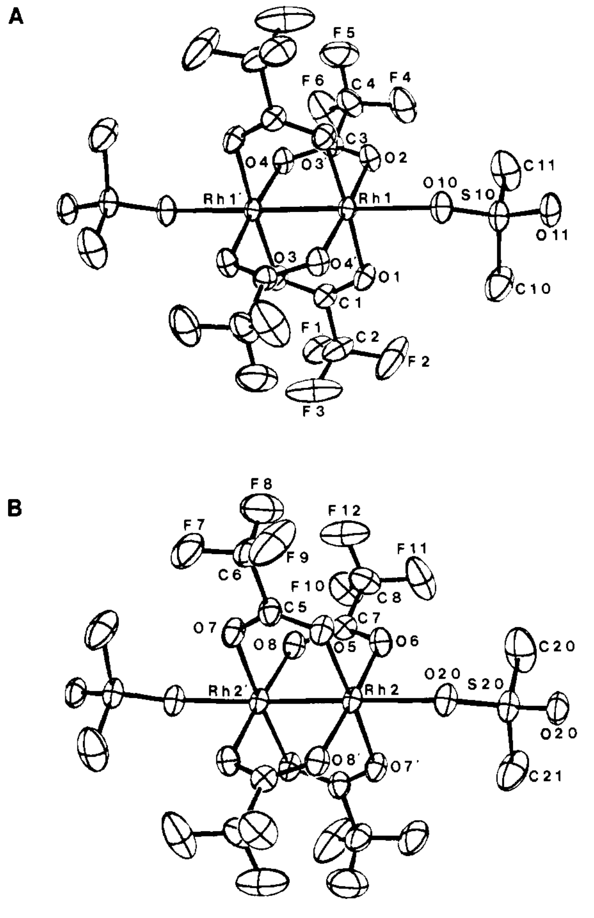

Figure 1. ORTEP drawing showing each of the two independent dinuclear units (molecules A and B) in $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$ with thermal ellipsoids drawn at the 40% probability level. Each molecule resides on a crystallographic center of inversion located at the midpoint of the Rh–Rh bond.

Lorentz and polarization effects and also for absorption with use of an empirical method based on ψ scans (ψ = 0–360° every 10°) for χ values near 90°. Eight sets of reflections ($0\bar{2}\bar{4}$, $\bar{1}\bar{3}4$, $0\bar{1}\bar{5}$, $\bar{1}\bar{4}\bar{3}$, $0\bar{4}\bar{2}$, $0\bar{5}\bar{5}$, $0\bar{3}\bar{6}$, $0\bar{4}\bar{4}$) were averaged to give an absorption profile with maximum, minimum, and average transmission values of 1.00, 0.91, and 0.94, respectively.

Structure Solution and Refinement.[32] The two independent Rh atom positions were derived with use of a combination of Patterson heavy-atom and direct methods. The observed structure factors were placed on an absolute scale with the aid of a Wilson plot. Six cycles of least-squares refinement of the two Rh atom positions with isotropic temperature factors gave residuals of

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.42$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2} = 0.51$$

Subsequent difference Fourier maps followed by least-squares refinement led to the location of all 40 nonhydrogen atoms in the asymmetric unit. With anisotropic thermal parameters assigned to all nonhydrogen atoms, the structure was refined to convergence with use of 3682 data having $I > 3\sigma(I)$ with $p = 0.05$. Final discrepancy factors were $R_1 = 0.048$ and $R_2 = 0.068$ with the esd of an observation of unit weight having a value of 2.158. With 361 variable parameters the final least-squares cycle had the largest shift-to-error ratio for a variable parameter equal to 0.26. The final data-to-parameter ratio was 3682:361 or 10.2:1. A final difference Fourier map revealed no peaks of structural significance. An inspection of observed and calculated structure factors gave no evidence for significant extinction effects. A table of the observed and calculated structure factor amplitudes is available for data with $I > 3\sigma(I)$.[33]

Infrared Spectra. These were recorded on a Pye Unicam SP1000 infrared spectrophotometer as suspensions in mineral oil and were calibrated with polystyrene film.

Results

The structure consists of two crystallographically independent molecules (A and B) each having the formula $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$. The molecules are illustrated in Figure 1 along with the atomic numbering scheme. Each molecule lies on a crystallographic center of inversion; molecule A is on the origin while molecule B resides at ($^1/_2$, $^1/_2$, $^1/_2$). There are no significant structural differences between the two molecules. Such differences as do occur between most equivalent dimensions are less than 3 times the estimated standard deviations of those dimensions. Table I records the positional and thermal parameters for the two molecules, and Table II presents the bond distances and angles.

Coordination about Rhodium. Each of the two independent Rh atoms, Rh(1) and Rh(2), is in a distorted octahedral geometry that is well-known for dimetal carboxylate complexes. The Rh–Rh bond distances are nearly the same with values of 2.401 (1) and 2.399 (1) Å for molecules A and B, respectively. The four bridging trifluoroacetate groups about the Rh–Rh bond provide four equatorial oxygen atoms for each Rh atom which coordinate with an average distance of 2.031 (3) Å. The range of Rh–O(carboxylate) distances extends only from 2.021 (3) to 2.038 (3) Å. The Rh–Rh–O(carboxylate) angles have a mean value in both molecules of 88.00 (9)°, individual angles being in the range 87.54 (9) to 88.47 (9)°. The four carboxylate oxygen atoms about each Rh atom define a square plane (Table III[33]) from which the Rh atoms are displaced 0.071 and 0.070 Å (for molecules A and B, respectively) toward the axial sulfone oxygen atoms. In molecules A and B these sulfone oxygen atoms are located 2.291 (3) and 2.284 (3) Å from each Rh atom, respectively, with only slight deviations from colinearity with the Rh–Rh vectors. The Rh–Rh–O(sulfone) angles are 179.67 (8) and 179.21 (9)° in A and B, respectively.

The carbon and oxygen atoms of the bridging trifluoroacetate groups are planar (Table III[33]). The two unique carboxyl group planes within each molecule A and B intersect at dihedral angles of 91.9 and 91.6°, respectively. The mean C–F, C–O, and C–C bond distances of the trifluoroacetate groups are 1.310 (8), 1.251 (6), and 1.540 (6) Å, respectively. The average O–C–O and F–C–F angles are 128.9 (4) and 108.0 (5)°.

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(32) 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.

(33) Supplementary material.

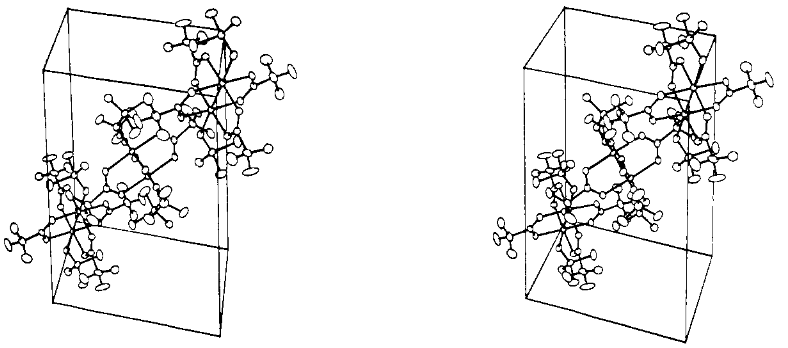

Figure 2. Stereoview of the contents of the unit cell of $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$. The view is approximately down the *c* axis with the *b* axis vertical, the *a* axis horizontal, and the origin located at the front upper left corner of the unit cell. Vibrational ellipsoids are drawn at the 20% probability level.

Sulfone Geometry. The sulfur atoms of the two unique coordinated sulfone groups display a distorted tetrahedral coordination. The S–C bond lengths vary from 1.757 (6) to 1.770 (6) Å with a mean value of 1.764 (4) Å. The mean of the S–O distances to the coordinated oxygen atoms is 1.455 (3) Å, while the mean distance for the uncoordinated S–O bonds is 1.450 (4) Å; the difference is not statistically significant. The mean sulfone angles for O–S–O, O–S–C, and C–S–C have values of 115.5 (2), 109.3 (3), and 103.5 (4)°, respectively.

Molecular Packing. Figure 2 provides a stereoscopic drawing of the unit cell contents of $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$. The figure shows one dinuclear unit of molecule B on the crystallographic center of inversion at ($^1/_2$, $^1/_2$, $^1/_2$) while two dinuclear units of molecule A flank molecule B on inversion centers at (1, 0, 0) and (0, 1, 1). No simple operation relates the two independent molecules to one another. The equatorial carboxylate oxygen planes of the two molecules form a dihedral angle of 37.1° (Table III[33]). The absence of any acidic hydrogen atoms within $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$ precludes intermolecular hydrogen bonding. Between dinuclear units only two fluorine–fluorine contacts are shorter than 3 Å: F(2)···F(10) = 2.933 Å and F(8)···F(11) = 2.978 Å.

Discussion

The compound reported here constitutes the first example, so far as we are aware, of a structurally confirmed sulfone complex. Only in $Cu_3Cl_6(H_2O)_2(TMSO)_2$[29] and $Na(C_6H_5SO_2)_2N$[34] have there previously been any known internuclear distances from a sulfone (or sulfone-like) oxygen atom to a cation, but in these two cases the distances 2.608 (11) and 2.342 (5) Å, respectively, imply only weak interactions. In the sodium compound we are not really dealing with a complex in the proper sense of the word, anyhow, but only with the interionic contacts which are an inherent part of an ionic crystal structure.

In $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$ each rhodium atom is bonded to a sulfone oxygen atom, with a mean Rh–O distance of 2.287 (3) Å. The structure of this molecule will now be compared with those of a number of related substances including other sulfones, sulfoxides, and other $Rh_2(O_2CR)_4L_2$ compounds.

Structural data for some sulfone compounds are collected in Table IV. By analogy with the well-known behavior of sulfoxides in their complexes, coordination of a sulfone oxygen atom might be expected to decrease the S–O bond order and hence lengthen the S–O bond. While this may seem to be the case in comparing the S–O bond lengths in $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$ and free Me_2SO_2,[35,36] the difference (0.007 Å) is scarcely significant. In a broad survey of organic sulfone molecules[37] an average S–O distance of 1.439 ± 0.014 Å is given for 30 solid-state structures investigated with use of X-ray crystallography. Although comparison with this number would suggest that the difference between S–O bond lengths in coordinated and uncoordinated sulfone groups might be 0.014 Å, the entire range from 1.39[34] to 1.49 Å[37] in the S–O bond lengths is so broad as to invalidate the comparison. Instead, it suggests that effects due to weak hydrogen bonding or crystal lattice packing forces may be at least as important in determining the S–O bond length as is direct coordination of one of the sulfone oxygen atoms. It should also be noted that in $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$, virtually no difference exists between the S–O bond lengths for coordinated and uncoordinated oxygen atoms.

A comparison of the sulfur bonding and geometry in $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$ with very similar structures of dimethyl sulfoxide (Me_2SO) adducts of $Rh_2(O_2CR)_4(Me_2SO)_2$ (R = CH_3[13] or CF_3[15]) provides some possible insight into the much greater number of compounds encountered containing coordinated Me_2SO as compared to Me_2SO_2. For one thing, the electron pair on the sulfur atom in Me_2SO permits coordination through either sulfur or oxygen atoms, and indeed this is observed for the dirhodium carboxylates with R = CH_3 or CF_3, respectively. In Me_2SO_2 this same lone pair is involved in bonding to another oxygen atom leading to a pair of relatively strong S–O bonds (1.453 (4) Å). The Me_2SO compounds show not nearly as short S–O bond distances with values of 1.477 (5) and 1.525 (3) Å for the $Rh_2(O_2CCH_3)_4$ and $Rh_2(O_2CCF_3)_4$ adducts, respectively. The longer S–O distance in $Rh_2(O_2CCF_3)_4(Me_2SO)_2$ leads to a correspondingly shorter axial Rh–O(Me_2SO) distance (2.236 (3) Å) than for that found in $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$ which has a mean axial Rh–O(Me_2SO_2) distance of 2.287 (3) Å. A comparison of the O–S–C and C–S–C angles in these two compounds also reflects the influence of the sulfur atom lone pair in Me_2SO. Average angles in the coordinated sulfone compound are 109.3 (3) and 103.5 (4)° while the corresponding sulfoxide adduct shows angles of 106.4 (2) and 98.5 (3)°. The reduction in the size of the angles in the Me_2SO compound is a result of the valence-shell electron pair repulsion effect[38] which tends to maximize the volume occupied by the sulfur lone pair leading to smaller angles between the other atoms coordinated to sulfur. When the sulfur lone pair is used in coordination as

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it is in $Rh_2(O_2CCH_3)_4(Me_2SO)_2$,[13] the O-S-C and C-S-C angles open up to values of 107.7 (2) and 100.4 (3)°, respectively, which, however, still fall short of the corresponding Me_2SO_2 angles.

A comparison of the infrared spectrum of $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$ with those of $Rh_2(O_2CCF_3)_4(H_2O)_2$ and Me_2SO leads straightforwardly to the following assignment of the S-O stretching frequencies of the coordinated dimethyl sulfone: a strong doublet with maxima at 1113 and 1124 cm^{-1} and a broad band at 1270 cm^{-1} with a shoulder at ca. 1290 cm^{-1}. The breadth and multiplicity of these bands is not unexpected since the spectrum was recorded on a solid sample and there are two crystallographically independent molecules in the unit cell. The positions of these bands may be compared with the following assignments[39] for dimethyl sulfone itself: $\nu_{sym} = 1143$ cm^{-1}, $\nu_{asym} = 1307$ cm^{-1}. A small lowering of the frequencies is consistent with weak coordination of the oxygen atom. In contrast, the longer S-O bond lengths found in $Rh_2(O_2CR)_4(Me_2SO)_2$ compounds show SO stretching frequencies[15] at lower energies: 1085 cm^{-1} (R = CH_3, S-bonded Me_2SO) and 939, 943 cm^{-1} (R = CF_3, O-bonded Me_2SO).

The dimethyl sulfone adduct of $Rh_2(O_2CCF_3)_4$ reported here is the third such structure of the general type $Rh_2(O_2CCF_3)_4L_2$ to be reported. The two previous compounds have been reported with L = C_2H_5OH[40] and Me_2SO.[15] In the ethanol adduct, two crystallographically independent $Rh_2(O_2CCF_3)_4(C_2H_5OH)_2$ molecules are present in the unit cell with Rh-Rh distances of 2.396 (2) and 2.409 (2) Å and Rh-O-(C_2H_5OH) distances of 2.26 (1) and 2.28 (1) Å, respectively. While these distances are quite similar to those found in the Me_2SO_2 adduct reported here, the packing of the $Rh_2(O_2CCF_3)_4L_2$ units involves a hydrogen-bonded network of ethanol molecules. The equatorial planes of the carboxylate oxygen atoms in the two independent molecules are nearly orthogonal, forming a dihedral angle of 88.7°. When L = Me_2SO_2, the carboxylate oxygen planes intersect with a much more acute dihedral angle of 37.1°, and in the compound with L = Me_2SO, the single independent Rh atom gives rise to parallel carboxylate oxygen planes. In both the Me_2SO_2 and C_2H_5OH adducts, the structures show little significant change either in the axial ligand dimensions or in the Rh-axial ligand bond lengths (average value 2.28 ± 0.01 Å) and Rh-Rh bond lengths (average value 2.401 ± 0.006 Å). However, the Me_2SO adduct clearly shows a shorter Rh-O(Me_2SO) distance (2.236 (3) Å), longer Rh-Rh distance (2.419 (1) Å, and concomitant lengthening of the S-O bond length from 1.513 (5) in free Me_2SO[41] to 1.525 (3) Å.

The variations in the dimensions of the above three structures of the type $Rh_2(O_2CCF_3)_4L_2$, where L is an oxygen-donor ligand, suggest a largely "σ only" interaction between the Rh and axial oxygen atoms which is consistent with results obtained from SCF-Xα-SW calculations on $Rh_2(O_2CH)_4(H_2O)_2$.[42] The inductive effect of the electronegative CF_3 groups in transmitted through the metal-ligand σ-bonding framework leading to a shorter Rh-axial ligand bond at the expense of the Rh-Rh bond length. In contrast, the structures of $Rh_2(O_2CR)_4(H_2O)_2$ (R = CH_3[43] and $C(CH_3)_3$[13]) clearly show that the effect of these electron-donating R groups is to give longer Rh-O(H_2O) distances (2.310 (3) and 2.295 (2) Å) and shorter Rh-Rh distances (2.3855 (5) and 2.371 (1) Å, respectively) relative to the corresponding $Rh_2(O_2CCF_3)_4L_2$ structural parameters. The similarity in donor ability of the axial oxygen atoms provides for a qualitative understanding of the bonding in this series of $Rh_2(O_2CR)_4L_2$ compounds. When the identity of the axial donor atom is changed to nitrogen, a much greater range of donor ability is accessible but changes in the energies of Rh-Rh bonding orbitals do not permit an a priori understanding of the observed[14] bond lengths involving the Rh atom. Such a detailed understanding in these dirhodium(II) systems will only be realized when structural results are augmented with probes (electronic absorption, photoelectron, and, where applicable, EPR spectroscopies in conjunction with quantum mechanical calculations) into the electronic structure which can unravel the nearly degenerate bonding and antibonding orbitals.

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Registry No. $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$, 77590-01-3; $Rh_2(O_2CCF_3)_4$, 31126-95-1.

Supplementary Material Available: Table III (least-squares planes and dihedral angles) and a table of observed and calculated structure factors for $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$ (18 pages). Ordering information is given on any current masthead page.

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