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Crystal and Molecular Structure of Tetrakis(benzoato)bis(dimethylsulfoxide)dirhodium(II)· toluene

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A considerable amount of work has been reported [1] on the structural properties of $Rh_2(RCO_2)_4L_2$ complexes, where RCO_2 is a bridging aliphatic carboxylate group and the L groups are monodentate ligands, but very little structural information exists for the corresponding aromatic carboxylate complexes. The dearth of such information prompted us to synthesize and characterize with X-ray diffraction techniques just such a compound, *viz.* tetrakis(benzoato)bis(dimethylsulfoxide)dirhodium(II), $Rh_2(C_6H_5CO_2)_4(Me_2SO)_2$. The crystal structure of the orange-colored complex reveals that both Me_2SO groups coordinate to the rhodium atoms through their S atoms.

Experimental

Synthesis

The starting material, $Rh_2(C_6H_5CO_2)_4(Me_2CO)_2$, was prepared by the method of Wilkinson [2]. These green crystals were dissolved in about 1 ml of THF and a few drops of DMSO were added. Then 1 ml of toluene was cautiously added to the surface of the THF solution. Single crystals suitable for structural analysis were grown by slow diffusion. The crystals of $Rh_2(C_6H_5CO_2)_4(Me_2SO_2)\cdot CH_3(C_6H_5)$ were orange colored.

Crystal Data

A single crystal of $Rh_2(C_6H_5CO_2)_4(Me_2SO)_2\cdot CH_3(C_6H_5)$, 0.32 × 0.25 × 0.12 mm in size, was selected for X-ray diffraction study and was mounted approximately along its longest dimension. An Enraf-Nonius CAD 4 diffractometer with graphite-monochromatized Mo Kα radiation was used for preliminary experiments and for the measurement of all diffraction intensities. The unit cell parameters are: triclinic, space group $P\bar{1}$, $a = 10.569(2)$, $b = 12.494(3)$, $c = 16.616(4)$ Å, $\alpha = 83.68(2)$, $\beta = 75.81(2)$, $\gamma = 67.82(2)^\circ$ (Niggli Cell, [3]), $V = 1969.4(9)$ Å^3, $Z = 2$, $D_c = 1.583$ g cm^3 and μ(Mo Kα) = 9.8 cm^{-1}.

A hemisphere of intensity data ($+h$, $\pm K$, $\pm l$) was collected with the θ–2θ scan mode. A variable scan width ($\Delta\omega^\circ = 0.7 + 0.34 \tan\theta$) and scan rate (between 2 and 20° min^{-1}) were used. Of the 4813 unique reflections measured ($0^\circ \leqslant 2\theta \leqslant 44^\circ$), 3225 had $I > 3\sigma(I)$. All diffraction intensities were corrected for Lorentz–polarization effects but not for absorption[†]. A 3% anisotropic decay correction factor was applied to the intensity data.

Normalized structure factor amplitudes for the 284 reflections with $|E| > 2.03$ were used in the computer program MULTAN. Three-dimensional E functions, phased by the solution with the largest combined figure of merit, 2.26, revealed the positions of the 10 O, 2 S, 2 Rh, and 6 ring C atoms; the remaining non-H atoms were located on subsequent Fourier difference syntheses. Several cycles of full-matrix least-squares refinement with anisotropic thermal parameters for all 53 non-H atoms (the H-atom positions were included in the structure factor calculations but were not refined) led to the final error indices: $R_1 = 0.035$, $R_w = 0.051$, and the goodness-of-fit = 1.563. The weights of the 3225 observations used in the least-squares refinements were equal to $[\sigma(F_o)]^{-2}$. The largest shift in a positional or thermal parameter in the final cycle of refinement was 0.35 of its e.s.d. A final difference Fourier synthesis showed no excursions above background. The final fractional coordinates are listed in Table I.

TABLE I. Fractional Atomic Coordinates of Nonhydrogen Atoms with e.s.d.s in Parentheses[a]

Atom	x	y	z
Rh(1)	0.24450(4)	0.27319(4)	0.32047(3)
Rh(2)	0.25163(4)	0.19090(4)	0.19449(3)
O(3)	0.2194(4)	0.1311(3)	0.3823(2)
C(4)	0.2217(6)	0.0501(5)	0.3410(4)
C(5)	0.2113(6)	−0.0558(5)	0.3878(4)
C(6)	0.2083(7)	−0.1462(6)	0.3478(4)
C(7)	0.2008(8)	−0.2443(5)	0.3901(5)
C(8)	0.1966(7)	−0.2549(6)	0.4726(5)
C(9)	0.1999(9)	−0.1692(6)	0.5134(5)
C(10)	0.2058(8)	−0.0689(6)	0.4724(4)
O(11)	0.2335(4)	0.0513(3)	0.2636(2)
O(12)	0.2707(4)	0.3359(3)	0.1334(2)

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[†] All crystallographic computing was done on a PDP 11/60 computer at the Molecular Structure Corp., College Station, Tex., with the Enraf-Nonius structure determination package with local modifications.

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TABLE I. *(continued)*

Atom	x	y	z
C(13)	0.2806(6)	0.4124(5)	0.1727(4)
C(14)	0.3000(6)	0.5149(5)	0.1234(4)
C(15)	0.3058(7)	0.5239(5)	0.0403(4)
C(16)	0.3153(9)	0.6188(7)	−0.0048(5)
C(17)	0.3217(8)	0.7092(6)	0.0339(5)
C(18)	0.3213(8)	0.6995(6)	0.1150(5)
C(19)	0.3086(7)	0.6035(6)	0.1607(4)
O(20)	0.2749(4)	0.4095(3)	0.2494(2)
O(21)	0.0325(4)	0.3515(3)	0.3338(3)
C(22)	−0.0247(6)	0.3286(5)	0.2829(4)
C(23)	−0.1806(6)	0.3774(5)	0.2981(4)
C(24)	−0.2592(6)	0.4548(5)	0.3611(4)
C(25)	−0.4023(7)	0.4967(6)	0.3770(4)
C(26)	−0.4690(6)	0.4613(6)	0.3293(5)
C(27)	−0.3933(7)	0.3857(6)	0.2660(4)
C(28)	−0.2494(6)	0.3436(6)	0.2514(4)
O(29)	0.0403(4)	0.2671(3)	0.2195(2)
O(30)	0.4648(4)	0.1200(3)	0.1773(3)
C(31)	0.5189(6)	0.1331(5)	0.2345(4)
C(32)	0.6748(6)	0.0797(5)	0.2201(4)
C(33)	0.7584(6)	0.0443(5)	0.1418(4)
C(34)	0.8995(7)	0.0023(6)	0.1292(4)
C(35)	0.9651(7)	−0.0072(7)	0.1941(5)
C(36)	0.8819(7)	0.0248(7)	0.2723(5)
C(37)	0.7399(7)	0.0696(6)	0.2853(4)
O(38)	0.4546(4)	0.1864(3)	0.3003(2)
S(39)	0.2382(2)	0.3502(1)	0.4516(1)
O(40)	0.2251(4)	0.4706(4)	0.4582(3)
C(41)	0.3879(8)	0.2600(7)	0.4884(5)
C(42)	0.1029(7)	0.3264(6)	0.5304(5)
S(43)	0.2529(2)	0.1174(1)	0.0639(1)
O(44)	0.2708(4)	−0.0043(3)	0.0540(3)
C(45)	0.0953(7)	0.2097(6)	0.0315(4)
C(46)	0.3801(7)	0.1517(6)	−0.0154(4)
C(47)[b]	0.3256(9)	0.3517(9)	−0.1820(7)
C(48)	0.1803(12)	0.4152(12)	−0.1404(8)
C(49)	0.0696(17)	0.4292(13)	−0.1351(8)
C(50)	0.0867(14)	0.3283(10)	−0.1961(8)
C(51)	0.2025(11)	0.2449(9)	−0.2412(7)
C(52)	0.3344(13)	0.2555(12)	−0.2376(8)
C(53)	0.4730(0)	0.1950(0)	−0.2700(0)

[a] See Fig. 1 for the identities of the atoms. [b] Atoms C(47) through C(53) belong to the disordered toluene molecule and are not shown in Fig. 1.

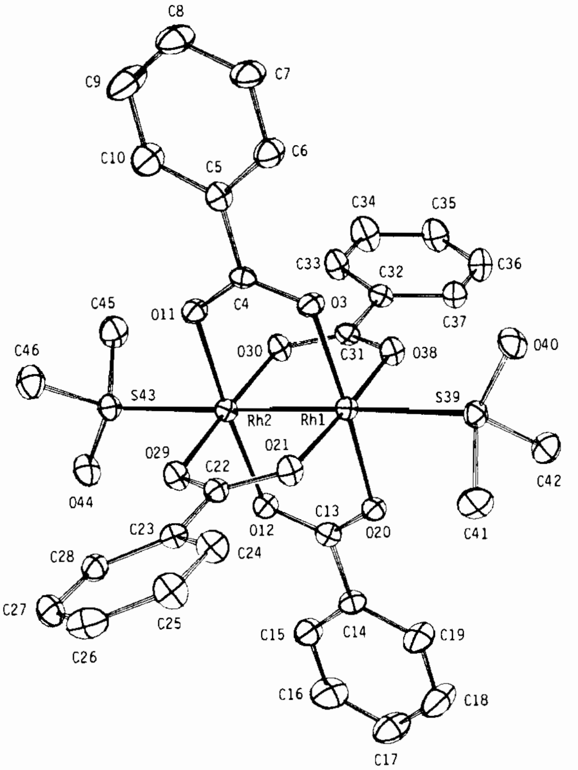

Fig. 1. An ORTEP drawing of $Rh_2(C_6H_5CO_2)_4(Me_2SO)_2$ with the atom labeling scheme given. Atoms C(47) through C(53) belong to the disordered toluene molecule and are not shown in the Figure. Ellipsoids of 25% probability are shown.

Results and Discussion

The structure of $Rh_2(C_6H_5CO_2)_4(Me_2SO)_2$ is shown in Fig. 1. A packing diagram is shown in Fig. 2. The molecule consists of a Rh_2^{4+} group bridged by four benzoate ligands, while the two remaining positions along the Rh–Rh bond axis are occupied by dimethyl sulfoxide molecules which coordinate with their S atoms; the molecule has no crystallographic symmetry. The Rh–Rh bond distance is 2.405(1) Å, while the mean Rh–S and Rh–O distances are 2.449(3) and 2.03(1) Å, respectively (see Table II). The Rh–Rh–S angles are within 3° of 180°, indicative of the near linear disposition of the S–Rh–Rh–S moiety. The dihedral angle between the two nearly perpendicular dibenzoate planes, consisting of the Rh atoms and atoms O(3)–O(20) and O(21)–O(38), is 88.6°. The mean S–O and S–C bond distances in the Me_2SO groups are 1.477(6) and 1.78(1) Å, respectively, and the six bond angles about each S atom are nearly tetrahedral (mean = 100°, range 99.9–122.8°), the C–S–C angles being somewhat compressed. The IR spectrum (KBr pellet) of the orange-colored crystals of this compound reveals a band at 1094(m) cm^{-1}, characteristic of the S–O stretching frequency of a S-ligated Me_2SO group [4].

The crystal structures of two other S bonded $Rh_2(RCO_2)_4(Me_2SO)_2$ carboxylate complexes have been reported, where R = CH_3 [1] and C_2H_5 [4]. The Rh–Rh and mean Rh–S bond distances are nearly identical to those in the benzoate structure: 2.406(1) and 2.451(1) Å (R = CH_3), and 2.407(1) and 2.449(1) Å (R = C_2H_5). Thus, the structural data for this particular family of compounds indicate that the

TABLE II. Bond Distances and Selected Bond Angles with e.s.d.s in Parentheses

A. Bond distances (Å)

Rh(1)–Rh(2)	2.405(1)	O(21)–C(22)	1.263(6)
		C(22)–C(23)	1.491(7)
		C(22)–O(29)	1.264(6)
Rh(1)–O(3)	2.025(3)	C(23)–C(24)	1.382(7)
Rh(1)–O(20)	2.046(4)	C(23)–C(28)	1.375(7)
Rh(1)–O(21)	2.043(4)	C(24)–C(25)	1.367(8)
Rh(1)–O(38)	2.029(4)	C(25)–C(26)	1.382(9)
Rh(1)–S(39)	2.454(2)	C(26)–C(27)	1.369(9)
		C(27)–C(28)	1.375(8)
Rh(2)–O(11)	2.025(3)	O(30)–C(31)	1.275(6)
Rh(2)–O(12)	2.031(3)	C(31)–C(32)	1.494(7)
Rh(2)–O(29)	2.023(4)	C(31)–O(38)	1.247(6)
Rh(2)–O(30)	2.044(4)	C(32)–C(33)	1.391(8)
Rh(2)–S(43)	2.443(2)	C(32)–C(37)	1.391(8)
		C(33)–C(34)	1.351(8)
O(3)–C(4)	1.273(6)	C(34)–C(35)	1.391(9)
C(4)–C(5)	1.487(7)	C(35)–C(36)	1.382(9)
C(4)–O(11)	1.260(6)	C(36)–C(37)	1.358(8)
C(5)–C(6)	1.386(8)		
C(5)–C(10)	1.386(8)	S(39)–O(40)	1.472(4)
C(6)–C(7)	1.363(8)	S(39)–C(41)	1.766(7)
C(7)–C(8)	1.354(9)	S(39)–C(42)	1.779(6)
C(8)–C(9)	1.345(9)		
C(9)–C(10)	1.375(9)	S(43)–O(44)	1.482(4)
		S(43)–C(45)	1.802(6)
O(12)–C(13)	1.264(6)	S(43)–C(46)	1.781(6)
C(13)–C(14)	1.497(8)		
C(13)–O(20)	1.258(6)	C(47)–C(48)	1.46(3)
C(14)–C(15)	1.362(8)	C(47)–C(52)	1.56(3)
C(14)–C(19)	1.368(8)	C(48)–C(49)	1.10(2)
C(15)–C(16)	1.355(9)	C(49)–C(50)	1.63(3)
C(16)–C(17)	1.390(10)	C(50)–C(51)	1.38(2)
C(17)–C(18)	1.339(10)	C(51)–C(52)	1.47(2)
C(18)–C(19)	1.380(9)	C(52)–C(53)	1.37(2)

B. Bond angles (°)

O(3)–Rh(1)–O(20)	175.4(2)	O(11)–Rh(2)–O(12)	175.5(1)
O(3)–Rh(1)–O(21)	90.3(2)	O(11)–Rh(2)–O(29)	89.4(2)
O(3)–Rh(1)–O(38)	88.1(2)	O(11)–Rh(2)–O(30)	90.6(2)
O(3)–Rh(1)–S(39)	89.7(1)	O(11)–Rh(2)–S(43)	94.9(1)
O(20)–Rh(1)–O(21)	90.8(2)	O(12)–Rh(2)–O(29)	90.7(2)
O(20)–Rh(1)–O(38)	90.5(2)	O(12)–Rh(2)–O(30)	88.9(2)
O(20)–Rh(1)–S(39)	94.7(1)	O(12)–Rh(2)–S(43)	89.5(1)
O(21)–Rh(1)–O(38)	175.1(1)	O(29)–Rh(2)–O(30)	175.5(1)
O(21)–Rh(1)–S(39)	92.4(1)	O(29)–Rh(2)–S(43)	91.2(1)
O(38)–Rh(1)–S(39)	92.2(1)	O(30)–Rh(2)–S(43)	93.3(1)
Rh(2)–Rh(1)–O(3)	88.2(1)	Rh(1)–Rh(2)–O(11)	87.6(1)
Rh(2)–Rh(1)–O(20)	87.4(1)	Rh(1)–Rh(2)–O(12)	88.0(1)
Rh(2)–Rh(1)–O(21)	88.1(1)	Rh(1)–Rh(2)–O(29)	87.2(1)
Rh(2)–Rh(1)–O(38)	87.2(1)	Rh(1)–Rh(2)–O(30)	88.3(1)
Rh(2)–Rh(1)–S(39)	177.87(4)	Rh(1)–Rh(2)–S(43)	177.05(4)
Rh(1)–O(3)–C(4)	118.7(3)	Rh(2)–O(11)–C(4)	119.7(3)
Rh(1)–O(20)–C(13)	119.5(4)	Rh(2)–O(12)–C(13)	119.5(4)
Rh(1)–O(21)–C(22)	118.7(4)	Rh(2)–O(29)–C(22)	120.7(3)
Rh(1)–O(38)–C(31)	120.0(3)	Rh(2)–O(30)–C(31)	117.6(4)

(continued)

TABLE II. *(continued)*

Rh(1)–S(39)–O(40)	121.8(2)	Rh(2)–S(43)–O(44)	122.8(2)
Rh(1)–S(39)–C(41)	108.5(2)	Rh(2)–S(43)–C(45)	107.6(2)
Rh(1)–S(39)–C(42)	109.1(2)	Rh(2)–S(43)–C(46)	107.8(2)
O(40)–S(39)–C(41)	107.5(3)	O(44)–S(43)–C(45)	108.1(3)
O(40)–S(39)–C(42)	107.2(3)	O(44)–S(43)–C(46)	108.2(3)
C(41)–S(39)–C(42)	100.8(3)	C(45)–S(43)–C(46)	99.9(3)

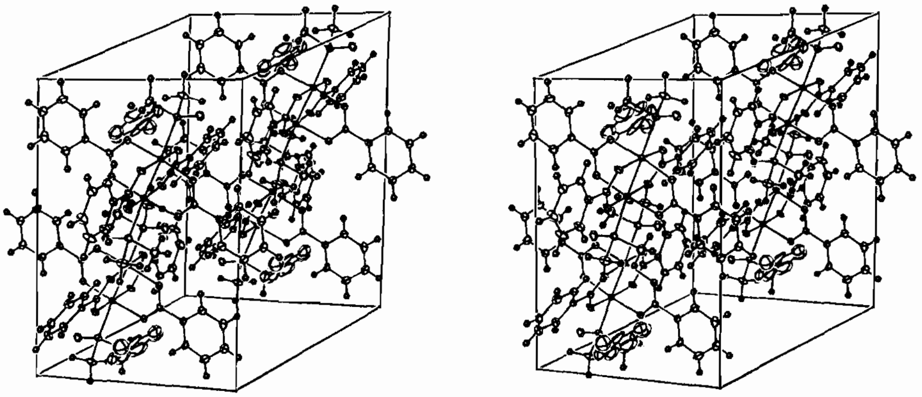

Fig. 2. Stereoscopic view of the packing diagram of $Rh_2(C_6H_5CO_2)_4(Me_2SO)_2 \cdot CH_3(C_6H_5)$ with thermal ellipsoids drawn at the 20% probability level. The view is approximately down the +*a* axis, with the +*b* axis extending horizontally to the right and the +*c* axis extending upwards.

Rh–Rh bond distance and overall coordination geometry are not discernibly changed if an aromatic R group is substituted for an aliphatic R group on the four bridging RCO_2 ligands*.

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*This conclusion may be premature; the Rh–Rh and mean Rh–N bond distances in $Rh_2(CH_3CO_2)_4(py)_2$, 2.3963(2) and 2.227(3) Å [5], are slightly different than those in $Rh_2(C_6H_5CO_2)_4(py)_2$, 2.402(1) and 2.234(7) Å [6].

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