

Bis(dimethyl sulfoxide-*S*)tetrakis(μ -*p*-hydroxybenzoato-*O*:*O'*)dirhodium(II)–tetrakis(μ -butyrato-*O*:*O'*)bis(dimethyl sulfoxide-*S*)dirhodium(II) cocrystal ethanol disolvate

Nikolay N. Sveshnikov, Michael H. Dickman* and Michael T. Pope

Department of Chemistry, Georgetown University, Box 571227, Washington, DC 20057-1227, USA

Correspondence e-mail: michaeld42@aol.com

Received 21 March 2000

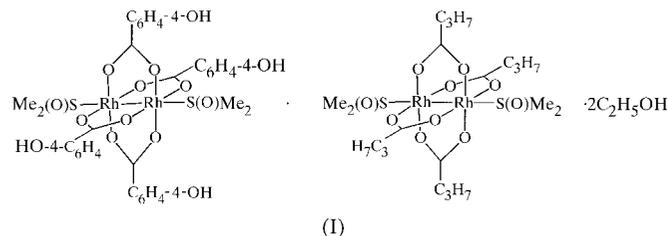
Accepted 13 July 2000

The title structure, $[\text{Rh}_2(\text{C}_7\text{H}_5\text{O}_3)_4(\text{C}_2\text{H}_6\text{OS})_2] \cdot [\text{Rh}_2(\text{C}_4\text{H}_7\text{O}_2)_4(\text{C}_2\text{H}_6\text{OS})_2] \cdot 2\text{C}_2\text{H}_6\text{O}$, contains two discrete neutral Rh–Rh dimers cocrystallized as the ethanol disolvate. Each dimer is situated on an inversion center. The butyrate chain displays disorder in one C-atom position. In each dimer, the dimethyl sulfoxide ligand (dmsO) is bound *via* S, as expected. The ethanol is a hydrogen-bond acceptor for one *p*-hydroxybenzoate hydroxyl group and acts as a hydrogen-bond donor to the dmsO O atom of a neighboring *p*-hydroxybenzoate dirhodium complex. A third hydrogen bond is formed from the other *p*-hydroxybenzoate hydroxyl group to the dmsO O atom of a butyrate–dirhodium complex.

Comment

Dirhodium(II) tetracarboxylate complexes have been extensively studied (Boyar & Robinson, 1983; Cotton & Walton, 1993). Our interest in the preparation of dirhodium(II) tetracarboxylates with functional organic groups is directed towards incorporation of these complexes into polyoxometalates. Recent success with incorporation of dirhodium(II) tetraacetate into $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ *via* hydrothermal techniques (Wei *et al.*, 1997; Wei, 1997) prompted us to investigate this reaction using other known dirhodium(II) carboxylates, as well as to synthesize novel dirhodium complexes. As part of this research, we prepared tetrakis(*p*-hydroxybenzoate)dirhodium(II), $[\text{Rh}_2(\text{C}_7\text{H}_5\text{O}_3)_4]$. Several dirhodium(II) tetracarboxylate crystal structures containing aromatic carboxylates have been reported (Li & Sun, 1981; Bancroft *et al.*, 1984; Cotton & Thompson, 1984; Simmons *et al.*, 1986; Callot *et al.*, 1989; Mehmet & Tocher, 1991). We report here the X-ray structure determination of an

advertentiously obtained single crystal of $[\text{Rh}_2(\text{C}_7\text{H}_5\text{O}_3)_4(\text{dmsO})_2]$ (dmsO is dimethyl sulfoxide) cocrystallized with $[\text{Rh}_2(\text{C}_4\text{H}_7\text{O}_2)_4(\text{dmsO})_2]$ as the ethanol disolvate, (I).



The Rh–Rh distances of 2.4102 (4) Å for the *p*-hydroxybenzoate molecule and 2.4037 (4) Å for the butyrate molecule in (I) are similar to those of the related compounds tetrakis(benzoato)bis(dmsO)dirhodium [2.405 (1) Å; Simmons *et al.*, 1986] and tetrakis(propionato)bis(dmsO)dirhodium [2.419 (1) Å; Cotton & Felthouse, 1980]. The Rh–S distances are also similar, with values of 2.4445 (6) and 2.4272 (7) Å for the two molecules of the present compound, compared with averages of 2.449 (8) and 2.449 (6) Å for the literature compounds. Angles around Rh in (I) are within 5° of 90 or 180°.

Two of the hydroxyl groups on the benzoate ligands donate protons to the O atoms of the dmsO ligands on the butyrate molecule, and the other two hydroxyl groups form hydrogen

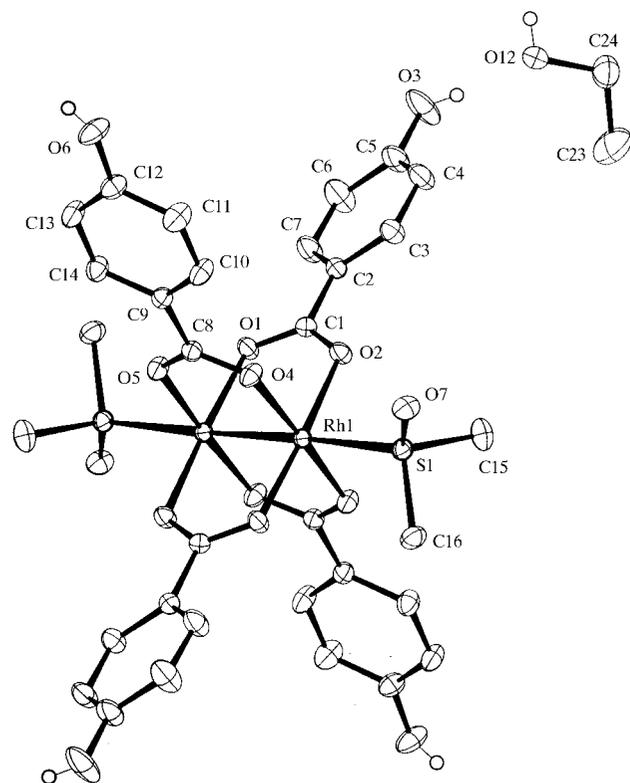


Figure 1

A view of the $[\text{Rh}_2(\text{C}_7\text{H}_5\text{O}_3)_4(\text{dmsO})_2]$ molecule in (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms bonded to C atoms have been omitted for clarity. One ethanol solvate molecule is shown.

bonds through ethanol molecules to the O atoms of the dmsu ligands on neighbouring benzoate molecules (Table 2).

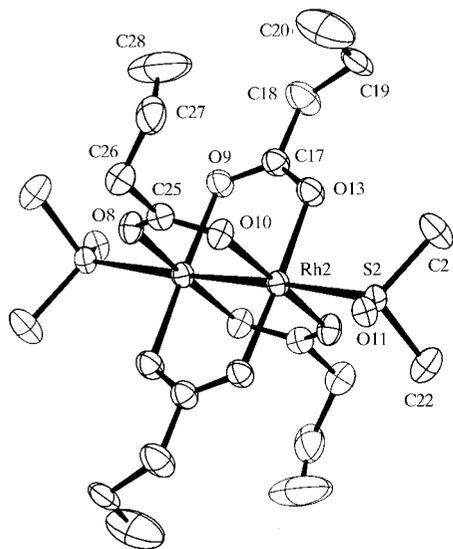


Figure 2
A view of the $[\text{Rh}_2(\text{C}_4\text{H}_7\text{O}_2)_4(\text{dmsu})_2]$ molecule in (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. The disordered C19A atom is not shown.

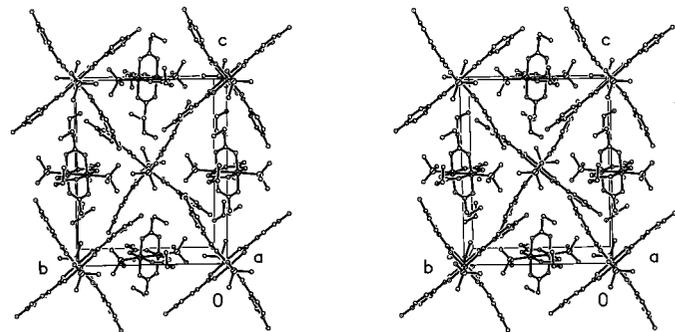


Figure 3
The stereopacking diagram for (I) viewed down the *a* axis.

Experimental

To prepare the *p*-hydroxybenzoate molecule, $[\text{Rh}_2(\text{C}_7\text{H}_5\text{O}_3)_4]$, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.25 g, 0.95 mmol) and 4-hydroxybenzoic acid (0.52 g, 3.8 mmol) were dissolved in ethanol–water (10 ml; 1:1) and heated at 333–343 K for 1 h. The mixture was cooled to room temperature and evaporated to dryness using a rotary evaporator. Excess 4-hydroxybenzoic acid and unreacted rhodium chloride were removed by washing with three hot 10 ml portions of water–ethanol (10:1). The green product was dried in a vacuum oven at 313 K for 24 h (yield 0.11 g, 28%, based on Rh). The purity of the compound obtained was checked by ^1H and ^{13}C NMR methods, using 5 mm tubes in a Bruker AM 300 NMR spectrometer operating at 300.13 and 75.47 MHz, respectively. ^1H NMR (CD_3OD , δ , p.p.m., *AA'BB'* system): 6.60–6.63 (*m*), 7.45–7.77 (*m*); ^{13}C NMR (CD_3OD , δ , p.p.m.): 115.65 (*d*, CH), 125.39 (*s*, CCOO), 132.23 (*d*, CH), 162.39 (*s*, COH), 186.26 (*s*, COO). Tetra- μ -butyrato-dirhodium(II), $[\text{Rh}_2(\text{C}_4\text{H}_7\text{O}_2)_4]$, was prepared according to literature methods (Behrens *et al.*, 1985; Drago *et al.*,

1979; Cotton & Shiu, 1986). Slow evaporation of an ethanol solution of a mixture of $[\text{Rh}_2(\text{C}_7\text{H}_5\text{O}_3)_4]$ and $[\text{Rh}_2(\text{C}_4\text{H}_7\text{O}_2)_4]$ with the addition of some drops of dimethyl sulfoxide adventitiously produced crystals of (I) in a recycling container. Crystals of the pure tetra-benzoate dimer were also obtained and X-ray data were collected. However, after partial refinement, it became clear that the axial ligands, water and ethanol, were disordered. Poor data quality prevented further refinement ($R_1 > 10\%$) and the structure was abandoned.

Crystal data

$[\text{Rh}_2(\text{C}_7\text{H}_5\text{O}_3)_4(\text{C}_2\text{H}_6\text{OS})_2] \cdot [\text{Rh}_2(\text{C}_4\text{H}_7\text{O}_2)_4(\text{C}_2\text{H}_6\text{OS})_2] \cdot 2\text{C}_2\text{H}_6\text{O}$
 $M_r = 1713.12$
Monoclinic, $P2_1/n$
 $a = 11.9418$ (6) Å
 $b = 15.2880$ (8) Å
 $c = 19.0307$ (10) Å
 $\beta = 90.915$ (1)°
 $V = 3473.9$ (3) Å³
 $Z = 2$

$D_x = 1.638$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 6450 reflections
 $\theta = 4.81$ – 56.51 °
 $\mu = 1.13$ mm⁻¹
 $T = 173$ (2) K
Block, red
0.22 × 0.20 × 0.14 mm

Data collection

SMART CCD area-detector diffractometer
 ω scans
38 253 measured reflections
8473 independent reflections
7201 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$
 $\theta_{\text{max}} = 28.32$ °
 $h = -15 \rightarrow 15$
 $k = -20 \rightarrow 20$
 $l = -24 \rightarrow 24$
Intensity decay: <2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.079$
 $S = 1.02$
8473 reflections
433 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 3.15P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.54$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.97$ e Å⁻³

Table 1

Selected geometric parameters (Å).

Rh1–O1	2.0280 (16)	Rh2–O8 ⁱⁱ	2.0230 (19)
Rh1–O4	2.0335 (16)	Rh2–O9	2.0350 (19)
Rh1–O5 ⁱ	2.0421 (16)	Rh2–O13 ⁱⁱ	2.040 (2)
Rh1–O2 ⁱ	2.0431 (16)	Rh2–O10	2.0462 (19)
Rh1–Rh1 ⁱ	2.4102 (4)	Rh2–Rh2 ⁱⁱ	2.4037 (4)
Rh1–S1	2.4445 (6)	Rh2–S2	2.4272 (7)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, -1 - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O3–H3O...O12	0.77 (3)	1.90 (3)	2.661 (3)	175 (5)
O6–H6O...O11 ⁱⁱ	0.75 (2)	1.95 (2)	2.699 (3)	175 (3)
O12–H12O...O7 ⁱⁱⁱ	0.73 (2)	1.95 (2)	2.679 (3)	176 (4)

Symmetry codes: (ii) $-x, -y, -1 - z$; (iii) $x - \frac{1}{2}, -\frac{1}{2} - y, \frac{1}{2} + z$.

H atoms connected to C atoms were placed in calculated positions using a riding model (C–H 0.95–0.99 Å). H atoms connected to O atoms were refined isotropically in observed positions, subject to a restraint of 0.82 (3) Å on the O–H distance. The rotations of the

dmsO methyl groups were varied. One of the butyrate chains showed slight disorder. Atom C19 occupies an alternative position, C19A. In order to model the disordered H atoms on C18 and C20, atoms C18A and C20A were utilized. Their coordinates and displacement parameters were constrained to be identical to those of C18 and C20.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1997a); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b); molecular graphics: *DIAMOND* (Bergerhoff, 1996) and *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We thank the National Science Foundation for support through grant No. CHE-9727417.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1540). Services for accessing these data are described at the back of the journal.

References

Bancroft, D. P., Cotton, F. A. & Han, S. (1984). *Inorg. Chem.* **23**, 2408–2411.

- Behrens, N. B., Carrera, G. M., Goodgame, D. M. L., Lawrence, A. S. & Williams, D. J. (1985). *Inorg. Chim. Acta*, **102**, 173–179.
- Bergerhoff, G. (1996). *DIAMOND*. Gerhard-Domagk-Strasse 1, Bonn, Germany.
- Boyar, B. E. & Robinson, S. D. (1983). *Coord. Chem. Rev.* **50**, 109–208.
- Bruker (1998). *SMART User's Manual*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Callot, H. J., Albrecht-Gary, A.-M., Al Joubbeh, M., Metz, B. & Metz, F. (1989). *Inorg. Chem.* **28**, 3633–3640.
- Cotton, F. A. & Felthouse, T. R. (1980). *Inorg. Chem.* **19**, 2347–2351.
- Cotton, F. A. & Shiu, K.-B. (1986). *Rev. Chim. Miner.* **23**, 14–19.
- Cotton, F. A. & Thompson, J. L. (1984). *Inorg. Chim. Acta*, **81**, 193–203.
- Cotton, F. A. & Walton, R. A. (1993). *Multiple Bonds Between Metal Atoms*, 2nd ed., pp. 431–501. Oxford: Clarendon Press.
- Drago, R. W., Tanner, S. P., Richman, R. M. & Long, J. R. (1979). *J. Am. Chem. Soc.* **101**, 2897–2903.
- Li, G. & Sun, Y. (1981). *Acta Chim. Sin.* **39**, 945–950.
- Mehmet, N. & Tocher, D. A. (1991). *Inorg. Chim. Acta*, **188**, 71–77.
- Sheldrick, G. M. (1990). *Acta Cryst. A* **46**, 467–473.
- Sheldrick, G. M. (1997a). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997b). *SHELXL97*. University of Göttingen, Germany.
- Simmons, C. J., Clearfield, A. & Sun, Y. (1986). *Inorg. Chim. Acta*, **121**, L3–6.
- Wei, X. (1997). PhD thesis, Georgetown University, Washington, DC, USA.
- Wei, X., Dickman, M. H. & Pope, M. T. (1997). *Inorg. Chem.* **36**, 130–131.