

## КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURES OF  
TETRAKIS(HYDROXYACETATO)bis(DIMETHYL-SULFOXIDE)DIRHODIUM(II)Q.-S. Ye<sup>1</sup>, M.-J. Xie<sup>2</sup>, J. Yu<sup>1</sup>, Q.-W. Chang<sup>1</sup>, J. Jiang<sup>1</sup>,  
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Tetrakis(hydroxyacetato)bis(dimethyl sulfoxide)dirhodium(II) (**1**) is synthesized by the reaction of dimethyl sulfoxide (DMSO) with  $\text{Rh}_2(\text{OOCCH}_2\text{OH})_4$ . The complex is characterized by elemental analysis, FT-IR, ESI<sup>+</sup>-MS, <sup>1</sup>H and <sup>13</sup>C NMR, along with single crystal X-ray diffraction. The ambidentate DMSO ligands are bound to the rhodium center of **1** through their sulfur atoms, which is firstly predicated by its orange color, then confirmed by the observation of an increase in the S—O stretching frequencies, and finally, unambiguously determined by single crystal X-ray diffraction. The structure of **1** contains two similar but crystallographically independent molecules. Both molecules contain lantern dirhodium units, joined equatorially by four bidentate hydroxyacetate ligands and two monodentate DMSO axial ligands. Four hydrogen bonds link the molecules together with  $d(\text{O}\cdots\text{O})$  of 2.767(4)—2.824(4) Å to form a three dimensional network.

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A considerable amount of works have now been published on the chemical and structural properties of dirhodium(II) tetracarboxylates with the general formula  $\text{Rh}_2(\text{OOCR})_4\text{L}_2$ , in which four carboxylates (the equatorial ligands) bridge the two rhodium atoms and L represents a Lewis base (the axial ligands) bound to the Rh—Rh axis [ 1—3 ]. Dirhodium(II) tetracarboxylates are quite stable and resistant to chemical disruption, thus they can be used to synthesize new carboxylates via equatorial ligand substitution or new adducts via axial ligand exchange [ 1, 2 ]. Due to the easy preparation [ 4 ], dirhodium tetraacetate is the most common starting material used for the synthesis of other dirhodium(II) tetracarboxylates. Accordingly, the chemical and structural properties of dirhodium tetraacetate and its adducts have been systematically studied [ 1, 2 ]. In contrast to the systematic exploration of dirhodium tetraacetate, less information is available about dirhodium tetrahydroxyacetate, although the equatorial ligand hydroxyacetate is an obvious derivative of acetate. Only recently, Sakai et al. reported the synthesis and structure of  $\text{Rh}_2(\text{OOCCH}_2\text{OH})_4(\text{H}_2\text{O})_2$  [ 5 ].

Dimethyl sulfoxide (DMSO) is an ambidentate ligand, which has been demonstrated by its complexes with dirhodium tetracarboxylates,  $\text{Rh}_2(\text{OOCR})_4$  [ 6—9 ]. The mode of DMSO coordination is dependent on the nature of the carboxylate R group substituent. It has been shown that more electron-donating substituents (R = Me, Et, Pro, Ph, C<sub>6</sub>H<sub>4</sub>—4-OH) [ 6—9 ] cause the rhodium atom to prefer the coordination of DMSO through their sulfur atoms, whereas the strongly electron-withdrawing substituent (R = CF<sub>3</sub>) [ 6 ] changes the preference to the oxygen atom. To the best of our knowledge,  $\text{Rh}_2(\text{OOCF}_3)_4$  is the only dirhodium tetracarboxylate coordinated to the O atoms of the DMSO

ligands. It is not clear that whether other electron-withdrawing substituents, such as OH, have similar properties as the fluorine substituents or not. In this context, we have investigated the reaction of  $\text{Rh}_2(\text{OOCCH}_2\text{OH})_4$  and DMSO. Now, we report the synthesis, characterization, and crystal structure of the DMSO adducts of  $\text{Rh}_2(\text{OOCCH}_2\text{OH})_4$ .

**Experimental. Synthesis of tetrakis(hydroxyacetato)bis(dimethyl sulfoxide)dirhodium(II) (1).** Tetrakis(hydroxyacetato)dirhodium(II) (0.51 g, 1.0 mmol) was dissolved in 10 ml of 4:1 water-DMSO and the resulting red solution was allowed to evaporate slowly at room temperature. Two weeks later, orange plate-like crystals precipitated. Yield: 0.43 g (64 %). Anal. Calcd. for  $\text{C}_{12}\text{H}_{24}\text{O}_{14}\text{Rh}_2\text{S}_2$ : C 21.76, H 3.65. Found: C 21.6, H 3.6. ESI<sup>+</sup>-MS (in MeOH)  $m/z$ : 529,  $[\text{M} - 2\text{DMSO} + \text{Na}]^+$ ; 607,  $[\text{M} - 2\text{DMSO} + \text{Na}]^+$ ; 1035,  $[2\text{M} - 4\text{DMSO} + \text{Na}]^+$ . IR (KBr,  $\text{cm}^{-1}$ ): 3426 (s), 2975 (w), 2939 (w), 1603 (s), 1418 (m), 1346 (m), 1223 (w), 1069 (m). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  5.19 (t, 4H, OH), 3.73 (d, 8H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  60.91 (CH<sub>2</sub>), 193.22 (COO).

**X-ray diffraction analysis.** Single crystals of **1** were obtained as described above. Intensity data for a single crystal (size 0.20×0.17×0.10 mm) was collected at room temperature on BRUKER SMART APEX II equipped with a CCD detector using graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.071073$  nm) in the  $\theta$  range from 1.39° to 28.38°. In total, 13313 reflections were measured. Crystallographic data:  $a = 14.701(2)$  Å,  $b = 12.074(2)$  Å,  $c = 12.103(2)$  Å,  $\beta = 92.221(1)^\circ$ , space group  $P2(1)/c$ ,  $V = 2146.6(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calc}} = 2.049$  g/cm<sup>3</sup>. The crystal structure was solved by a direct method. The crystalline phase has the composition  $\text{Rh}_2(\text{OOCCH}_2\text{OH})_4[(\text{CH}_3)_2\text{SO}]_2$ . The final full-matrix refinement on 5013 independent reflections led to  $R_1 = 0.0499$  ( $wR_2 = 0.0689$ ). For 3656 reflections with  $I > 2\sigma(I)$ :  $R_1 = 0.0312$  ( $wR_2 = 0.0623$ ). The *S*-factor against  $F^2$  is 0.995. All calculations were made using the SHELXTL-97 software [ 10 ]. The CIF file with complete information about the structure was deposited at CCDC (No. 769413), from which it is available free of charge on request at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Selected geometrical parameters are given in Table 1. The hydrogen bonds are characterized in Table 2.

**Results and discussion.** Complex **1** was synthesized by the addition of DMSO to an aqueous solution of  $\text{Rh}_2(\text{OOCCH}_2\text{OH})_4$ . The reaction occurred immediately, indicated by a color change from blue to orange-red [ 2 ].

The complex was characterized by elemental analysis, FT-IR, ESI<sup>+</sup>-MS, <sup>1</sup>H and <sup>13</sup>C NMR. The elemental analysis data are in good agreement with the calculated values. It shows three peaks at  $m/z$

T a b l e 1

Bond lengths (*d*, Å), bond angles ( $\omega$ , deg.) for **1**

Bond	<i>d</i>	Bond	<i>d</i>	Bond	<i>d</i>
Rh(1)—O(4)	2.031(2)	S(1)—O(14)	1.478(3)	Rh(2)—O(12)	2.030(2)
Rh(1)—O(5)	2.039(2)	Rh(1)—Rh(1)#2	2.4077(5)	Rh(2)—S(2)	2.4331(9)
Rh(1)—O(6)	2.043(2)	Rh(2)—O(1)	2.032(2)	Rh(2)—Rh(2)#1	2.4096(5)
Rh(1)—O(7)	2.037(2)	Rh(2)—O(2)	2.023(2)	S(2)—O(10)	1.488(3)
Rh(1)—S(1)	2.4565(9)	Rh(2)—O(11)	2.048(2)		
Angle	$\omega$	Angle	$\omega$	Angle	$\omega$
O(4)—Rh(1)—O(6)	88.97(10)	O(4)—Rh(1)—O(7)	175.53(9)	O(1)—Rh(2)—O(11)	88.10(10)
O(4)—Rh(1)—O(5)	91.06(10)	Rh(1)#2—Rh(1)—S(1)	177.54(3)	O(2)—Rh(2)—O(11)	175.44(9)
O(7)—Rh(1)—O(5)	88.67(10)	O(2)—Rh(2)—O(1)	91.66(10)	O(12)—Rh(2)—O(1)	175.44(9)
O(7)—Rh(1)—O(6)	90.94(10)	O(2)—Rh(2)—O(12)	88.99(10)	Rh(2)#1—Rh(2)—S(2)	178.00(3)
O(5)—Rh(1)—O(6)	175.38(9)	O(12)—Rh(2)—O(11)	90.90(10)		

Symmetry code: #1:  $-x+1, -y+1, -z$ ; #2:  $-x, -y+1, -z$ .

Hydrogen bonds for **1**

No.	D—H...A bond	Distances, Å			DHA angle, deg.	Position of the A atom
		D—H	H...A	D...A		
1	O(13)—H(15)...O(9)	0.82	2.00	2.820(4)	173.3	$-x, -y+1, -z$
2	O(9)—H(9)...O(14)	0.82	1.99	2.767(4)	157.6	$x, -y+1/2, z-1/2$
3	O(8)—H(8)...O(10)	0.82	1.99	2.798(3)	170.3	$-x+1, -y+1, -z$
4	O(3)—H(3)...O(8)	0.82	2.01	2.824(4)	172.5	$-x+1, -y+1, -z$

529, 607, and 1035 which can be assigned to the  $[M - 2\text{DMSO} + \text{Na}]^+$ ,  $[M - 2\text{DMSO} + \text{Na}]^+$ , and  $[2M - 4\text{DMSO} + \text{Na}]^+$  fragments respectively. It is noteworthy that **1** does not show a  $[M]^+$  peak, probably due to the low stability of the axial ligands under electron spray ionization, which is consistent with our previous observation for other adducts of dirhodium tetracarboxylates [11, 12]. Two signals at  $\delta$  5.19 and 3.73 ppm observed in the  $^1\text{H}$  NMR spectra are assigned to the OH and  $\text{CH}_2$  protons, respectively. It is worthy to note that there are two singlets at  $\delta$  2.53 and 2.49 ppm with the integral ratio of 1:1 observed in the  $^1\text{H}$  NMR spectra, which indicates a rapid exchange of the axial DMSO ligands with the deuterated DMSO solvent. Therefore, the two singlets can be attributed to the resonances of the bound and free DMSO ligands, respectively. The carbon resonances of DMSO also show two signals; one is a singlet at  $\delta$  40.42 ppm, which could be attributed to the bound DMSO ligand; another is a heptet ( $\delta$  40.14, 39.93, 39.72, 39.51, 39.31, 39.10, and 38.89 ppm), a well-known carbon resonances of free DMSO ligand. Two other carbon resonances ( $\delta$  60.91 and 193.22 ppm) observed in the  $^{13}\text{C}$  NMR spectra correspond to the  $\text{CH}_2$  and COO carbon atoms. The DMSO ligands in **1** are bound to the rhodium center through sulfur atoms, which is firstly predicated by the color of the reaction solution change from blue to orange-red [1, 2]. This coordination mode can be further confirmed by the observation of  $\nu_{\text{SO}}$  at  $1069\text{ cm}^{-1}$ , since the S—O stretching frequencies have been known for a long time to be diagnostic of the DMSO coordination mode [13]. It is found that the monodentate  $\eta$ -S coordination of DMSO causes an increase in the S—O stretching frequencies, whereas a decrease in the frequencies is observed in monodentate DMSO  $\eta$ -O, as compared to the free DMSO ligands [6–8]. The  $\nu_{\text{SO}}$  value of  $1069\text{ cm}^{-1}$  in **1** is  $14\text{ cm}^{-1}$  higher than that of free DMSO, in agreement with the  $\eta$ -S coordination of DMSO. It is noted that the  $\nu_{\text{SO}}$  value of **1** decreases by  $17\text{--}25\text{ cm}^{-1}$  as compared to the values of  $\text{Rh}_2(\text{OOCR})_4(\text{DMSO})_2$  ( $R = \text{Me, Et, Ph}$ ) [6–8], which may be attributed to the electron-withdrawing substituent (OH) in the carboxylate R group of **1**.

The structure of **1** was unambiguously determined by single crystal X-ray diffraction. A single crystal of **1** was grown by slow evaporation of an aqueous solution in the presence of DMSO over a period of two weeks. It crystallized from the solution in the form of monoclinic plate-like crystals. The ORTEP drawing of **1** along with the corresponding atom numbering is shown in Fig. 1, and selected bond distances and angles are listed in Table 1.

The structure of **1** contains two crystallographically independent molecules (*A* and *B*, Fig. 1). Each molecule has a crystallographic center of inversion at the midpoint of the Rh—Rh bond. There are no significant structural differences between the two molecules. Both molecules contain lantern dirhodium units, joined equatorially by four bidentate hydroxyacetate ligands and two monodentate DMSO axial ligands bonded to the rhodium atoms by the sulfur atoms. Each rhodium atom shows a slightly distorted octahedral environment having four equatorial positions occupied by the carboxylate oxygen atoms of the hydroxyacetate ligands; the axial sites are occupied by one sulfur atom of DMSO and by another Rh atom of the dirhodium unit.

The Rh—Rh bond lengths in the two independent molecules are similar (2.4077(5) and 2.4096(5) Å for molecules *A* and *B*, respectively). However, the Rh—S bond length in molecule *A*, 2.4565(9) Å, is 0.0234 Å longer than the value in molecule *B*, 2.4331(9) Å. Both Rh—Rh and Rh—S bond lengths are similar to the five related DMSO adducts of dirhodium(II) tetracarboxylates,

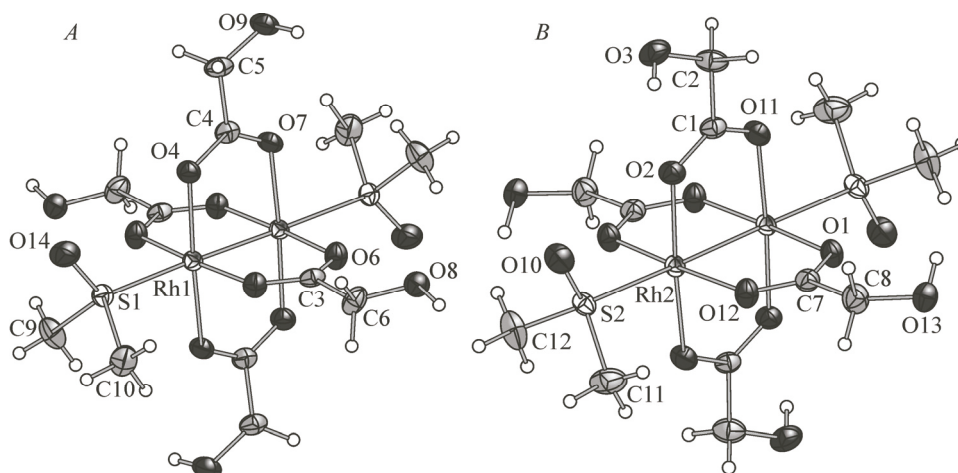


Fig. 1. ORTEP drawing showing each of the two independent dinuclear units (molecules *A* and *B*) in **1** with displacement ellipsoids at the 50 % probability level. Each molecule resides on a crystallographic center of inversion located at the midpoint of the Rh—Rh bond

$\text{Rh}_2(\text{OOCR})_4(\text{DMSO})_2$  ( $\text{R} = \text{Me}, \text{Et}, \text{Pro}, \text{Ph}, \text{C}_6\text{H}_4\text{—}4\text{—OH}$ ) [6–9]. The S—O bond distances (1.478(3) and 1.488(3) Å) of **1** are slightly shorter than the value of the free DMSO molecule [14], which are consistent with that the S coordination of DMSO to  $\text{Rh}_2(\text{OOCR})_4$  leading to a shortening of the S—O bond length. The range of Rh—O distances extends from 2.023(2) to 2.048(2) Å, agreeing well with the data of rhodium(II) carboxylates described in the literature [1, 2, 15].

The axial S—Rh—Rh—S chain is nearly linear with Rh—Rh—S angles of 175.53(9)° and 178.00(3)° for molecules *A* and *B*, respectively. The Rh—Rh—O angles have a mean value of 89.9°, individual angles being in the range from 88.1(1)° to 91.7(1)°. In both molecules, the two groups of four equatorial oxygen atoms are almost perfectly eclipsed with respect to each other with a maximum O—Rh—Rh—O torsion angle of 1°.

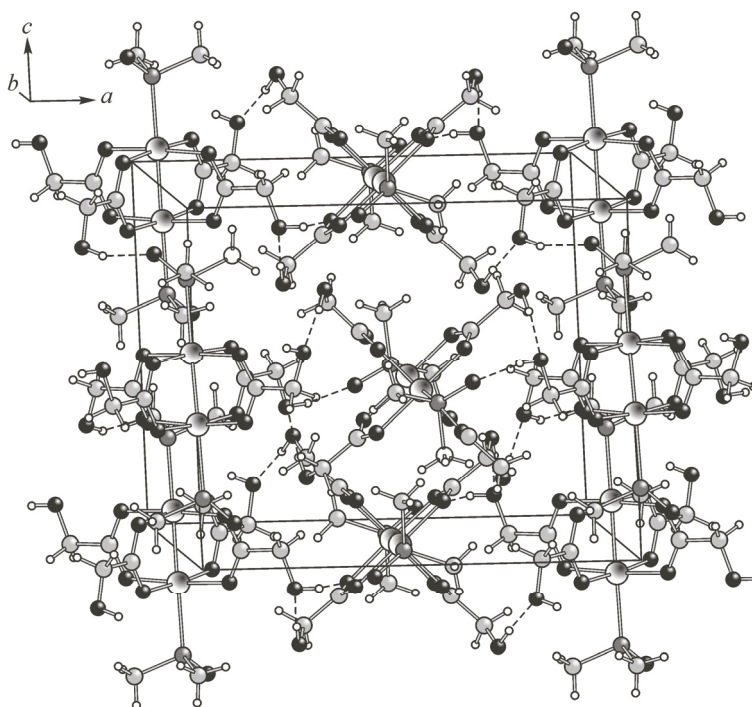


Fig. 2. Weak pairing of molecules of **1** within the unit cell

The hydroxyl groups of hydroxyacetates in **1** play an important role in the structural stacking by forming strong intermolecular O—H···O interactions. All the donors of the four hydrogen bonds are the hydroxyl groups, whereas the acceptors are the oxygen atoms of OH and DMSO (Table 1). The distances of the four hydrogen bonds are in the range from 2.767(4) to 2.824(4) Å. These interactions link the molecules together to form a three dimensional network (Fig. 2).

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