Crystal structure of acetopyruvato-κ^2O,O'-dicarbonylrhodium(I), $C_8H_7O_6Rh$

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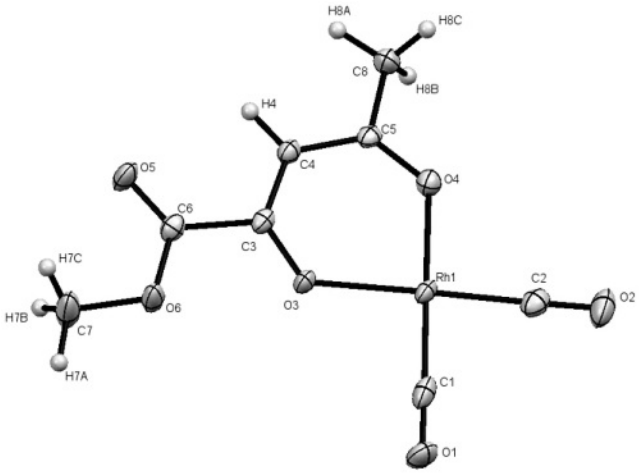

Abstract

$C_8H_7O_6Rh$, triclinic, $P\bar{1}$ (no. 2), a = 7.519(3) Å, b = 7.883(3) Å, c = 9.799(4) Å, α = 103.18(1)°, β = 110.93(1)°, γ = 99.95(1)°, V = 507.1 Å^3, Z = 2, $R_{gt}(F)$ = 0.0252, $wR_{ref}(F^2)$ = 0.0747, T = 100 K.

Table 1. Data collection and handling.

Crystal:	red needles, size 0.137×0.154×0.721 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	16.89 cm^{-1}
Diffractometer, scan mode:	Bruker APEX2, φ and ω
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8140, 2427
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2253
$N(param)_{refined}$:	136
Programs:	SADABS, SAINT, SIR92, SHELX, SHELXD, MERCURY, WinGX, publCIF, PARST95, PLATON [15–23]

Source of material

$RhCl_3 \cdot 3H_2O$ (0.011 g, 0.043 mmol) was refluxed in 2 ml of DMF until the red colour was observed to turn a brilliant yellow (approx. 30 min). The solution was then cooled in an ice-bath before adding acetopyruvate (0.00738 g, 0.0512 mmol) to the reaction mixture. The yellow product was precipitated by the addition of ice-water and was then collected by centrifugation. It was then recrystallized from acetone. Red needle-shaped crystals suitable for single crystal X-ray diffraction studies were obtained after approximately three days. (yield mass = 0.0071 g.; 55 %) **^{1}H-NMR** (600 MHz, methylene chloride-d_2; *ppm*): δ = 3.85 (s, 1H), 2.91 (s, 3H), 2.82 (s, 3H). **^{13}C-NMR** (151 MHz, methylene chloride-d_2; *ppm*): δ = 195.29, 168.09, 162.92, 101.71, 36.73, 28.47.

Experimental details

The methyl H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.95 Å and U_{iso}(H) = 1.5U_{eq}(C). The highest residual electron density was located 0.74 Å from Rh1 and the deepest hole was 0.85 Å from Rh1.

Discussion

Rhodium is one of the most studied transition metals due to its importance in various applications including catalysis and biological activity [1, 2]. Our interest in rhodium chemistry forms part of an over-arching investigation into steric manipulation of various transition metal complexes for application in catalysis, radiopharmaceutical and separation technology [3–10]. The title complex displays a typical square planar geometry with the rhodium centre surrounded by two carbonyl and a β-diketonato ligand. No significant distortion of the geometry is observed with the rhodium centre situated a mere 0.046 Å above the basal plane. There exists oxygen-oxygen contacts determined as 2.978(1) Å between the carbonyl groups of neighbouring molecules in a head-to-head configuration. Metallophilic interaction was observed between the rhodium centres of the molecules in the solid state. Metallophilicity has been defined as the interaction between electron densities of large metal centres with an associated energy in the same order as hydrogen-bonding [11]. These metallophilic interactions often lead to the construction of 1-D metal chains and have been widely recognized for other square-planar Rh(I) molecules [12]. The rhodium complex reported here showed stacking in such a way that the rhodium atoms of neighbouring complexes interact almost perpendicular to the coordination polyhedron, with Rh···Rh distances of 3.124(2) Å. These values are slighly shorter than the Rh···Rh distances reported for [Rh(*acac*)$(CO)_2$] (3.253 and 3.271 Å) [13]. For the benzoyl-1,1,1-trifluoroacetonatodicarbonylrhodium(I) complex these distances were reported as 3.537 Å [14]. Neighboring complexes arrange in a head to tail mode with a reported angle of 94.52° between the polyhedra of the rhodium centres. These interactions are the dominant force governing the packing of the molecules within the crystal structure. In contrast with previous structures the metallophillic interactions are only observed between two neighbouring rhodium centres and does not extend to form a infinite chain as reported for similar complexes [10,13].

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4)	2*i*	0.6261	0.8625	1.0614	0.021
H(8A)	2*i*	0.7331	0.9233	1.3209	0.037
H(8B)	2*i*	0.7189	0.7487	1.3779	0.037
H(8C)	2*i*	0.9297	0.8670	1.4018	0.037
H(7A)	2*i*	0.2943	0.5719	0.4082	0.059
H(7B)	2*i*	0.1946	0.6628	0.5144	0.059
H(7C)	2*i*	0.3887	0.7806	0.5118	0.059

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	2*i*	0.80715(2)	0.37389(2)	0.98992(2)	0.0153(1)	0.0125(1)	0.0235(1)	0.00681(9)	0.00845(9)	0.00726(9)
O(3)	2*i*	0.6563(3)	0.5033(2)	0.8485(2)	0.0194(8)	0.0150(9)	0.0189(8)	0.0094(7)	0.0075(7)	0.0058(7)
O(5)	2*i*	0.4369(3)	0.8532(3)	0.7975(2)	0.040(1)	0.022(1)	0.026(1)	0.0202(9)	0.0159(8)	0.0100(8)
O(6)	2*i*	0.4434(3)	0.6077(3)	0.6315(2)	0.037(1)	0.028(1)	0.0187(9)	0.0226(8)	0.0088(8)	0.0072(7)
O(1)	2*i*	0.7594(3)	0.0798(3)	0.7145(2)	0.039(1)	0.021(1)	0.030(1)	0.0153(9)	0.0155(9)	0.0044(8)
O(4)	2*i*	0.8271(3)	0.5666(3)	1.1793(2)	0.0200(9)	0.0197(9)	0.0222(9)	0.0069(7)	0.0074(7)	0.0069(7)
C(2)	2*i*	0.9344(4)	0.2516(4)	1.1176(3)	0.020(1)	0.019(1)	0.032(1)	0.005(1)	0.011(1)	0.009(1)
C(3)	2*i*	0.6145(3)	0.6500(3)	0.8969(3)	0.014(1)	0.014(1)	0.023(1)	0.0049(9)	0.0093(9)	0.0074(9)
C(4)	2*i*	0.6623(3)	0.7523(3)	1.0463(3)	0.016(1)	0.016(1)	0.021(1)	0.0066(9)	0.0078(9)	0.0062(9)
C(6)	2*i*	0.4889(3)	0.7181(3)	0.7716(3)	0.020(1)	0.019(1)	0.024(1)	0.008(1)	0.012(1)	0.009(1)
O(2)	2*i*	1.0139(3)	0.1790(3)	1.1984(3)	0.034(1)	0.032(1)	0.047(1)	0.0163(9)	0.012(1)	0.025(1)
C(1)	2*i*	0.7789(4)	0.1915(4)	0.8206(3)	0.020(1)	0.022(1)	0.035(2)	0.011(1)	0.012(1)	0.017(1)
C(8)	2*i*	0.7881(4)	0.8210(4)	1.3333(3)	0.028(1)	0.023(1)	0.019(1)	0.010(1)	0.005(1)	0.004(1)
C(5)	2*i*	0.7616(3)	0.7046(3)	1.1790(3)	0.013(1)	0.013(1)	0.023(1)	0.0021(9)	0.0056(9)	0.0041(9)
C(7)	2*i*	0.3204(5)	0.6599(5)	0.5065(3)	0.057(2)	0.046(2)	0.023(1)	0.039(2)	0.012(1)	0.012(1)

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