Crystal structure of tetrakis(μ_2-formiato-κ^2*O:O'*)bis(4-methylpyridine-κ*N*) dirhodium(II) (Rh–Rh), $C_{16}H_{18}N_2O_8Rh_2$

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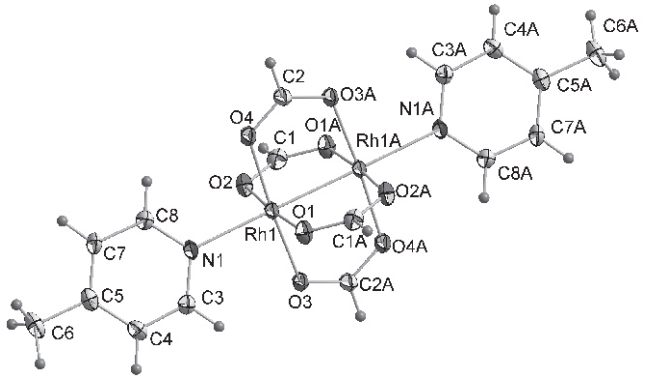

Abstract

$C_{16}H_{18}N_2O_8Rh_2$, monoclinic, $P2_1/c$ (no. 14), a = 10.635(2) Å, b = 11.375(3) Å, c = 7.854(2) Å, β = 90.634(3)°, V = 950.0 Å^3, Z = 2, $R_{gt(F)}$ = 0.0373, $wR_{ref(F^2)}$ = 0.0930, T = 100 K.

Table 1. Data collection and handling.

Crystal:	pink prisms, size 0.02×0.15×0.16 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	17.84 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8908, 2284
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1534
$N(param)_{refined}$:	128
Programs:	SHELX [12], DIAMOND [13]

Source of material

$Rh_2(O_2CH)_4(H_2O)_2$ (10 mg, 0.024 mmol) was dissolved in 5ml of distilled water. Slow vapor diffusion of 4-methylpyridine into the solution in two weeks yielded pink prism crystals suitable for crystallographic analysis.

Experimental details

The H atoms of the methyl were positioned geometrically (d(C–H) = 0.96 Å), and refined as riding with U_{iso}(H) = 1.5 U_{eq}(C). The other H atoms were positioned geometrically (d(C–H) = 0.93 Å), and refined as riding with U_{iso}(H) = 1.2 U_{eq}(C).

Discussion

A considerable amount of work [1–8] has now been reported on the chemical and structural properties of rhodium(II) carboxylates with general formula $Rh_2(OOCR)_4L_2$, in which L represents a Lewis base and R an organic group. Rhodium(II) carboxylates readily form adducts in which the axial sites are occupied by donor solvents or ligands, leading to the isolation of a large number of adducts. Compared to many adducts of dirhodium tetraacetate, however, crystal structures of dirhodium tetraformiate and its adducts are seldom reported [1, 8, 9]. The title complex crystallized in the form of purple prism crystals of monoclinic symmetry. The Rh atom is coordinated in a distorted octahedral manner. Each Rh atom is bound to four O atoms of the formiate ligands in the equatorial coordination plane, while the other two sites on the metal are occupied by one N atom of the 4-methylpyridine ligand and the second rhodium atom. The Rh–Rh bond length is 2.4044(9) Å, which is slightly longer than that found in adducts of dirhodium tetraformiate $Rh_2(OOCH)_4(H_2O)_2$ (2.38 Å) and $Rh_2(OOCH)_4(DMF)_2$ (2.3973(5) Å), and almost equivalent to that in $Rh_2(OOCCH_3)_4$(4-pyridinemethanol)$_2$ (2.4030(7) Å) [9–11]. The range of Rh–O distances ranges from 2.029(4) to 2.045(4) Å and the Rh–N distance is 2.241(4) Å, agreeing well with the data of rhodium(II) carboxylates [1, 8–11]. The Rh–Rh–O angles have a mean value of 89.9(7)°, individual angles being in the range 89.4(2) to 90.4(2)°. The four carboxylate oxygen atoms around Rh atom define a square plane from which the Rh atom is displaced by 0.0754(4) Å, toward the axial nitrogen atoms. The axial Rh–Rh–N angle is close to linear with a value of 179.26(9)°. The pyridine rings are planar with no deviations greater than 0.010 Å. The pyridine rings of neighbouring complexes are parallel to each other with a distance of 3.563 Å .

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.1400	0.0538	1.4056	0.055
H(2)	4*e*	0.0940	–0.2975	1.0278	0.055
H(3)	4*e*	0.2123	0.2098	0.6796	0.055
H(4)	4*e*	0.3970	0.2641	0.5503	0.061
H(6A)	4*e*	0.6841	0.1939	0.6559	0.091
H(6B)	4*e*	0.6122	0.2236	0.4810	0.091
H(6C)	4*e*	0.6632	0.0934	0.5159	0.091
H(7)	4*e*	0.5674	–0.0106	0.7767	0.056
H(8)	4*e*	0.3785	–0.0588	0.9002	0.051

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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)	4*e*	0.09762(3)	0.02452(4)	0.93266(5)	0.0208(2)	0.0300(2)	0.0418(2)	–0.0000(2)	0.0076(1)	–0.0016(2)
O(1)	4*e*	–0.0112(3)	0.0084(3)	1.2946(5)	0.035(2)	0.056(2)	0.039(2)	–0.003(2)	0.004(2)	–0.005(2)
O(2)	4*e*	0.1722(3)	0.0536(3)	1.1696(5)	0.029(2)	0.050(2)	0.048(2)	–0.006(2)	0.001(2)	–0.005(2)
O(3)	4*e*	0.0373(3)	0.1941(3)	0.9211(5)	0.030(2)	0.033(2)	0.059(2)	0.005(1)	0.017(2)	0.004(2)
O(4)	4*e*	0.1462(3)	–0.1485(3)	0.9529(5)	0.028(2)	0.033(2)	0.070(3)	0.004(2)	0.013(2)	–0.001(2)
N(1)	4*e*	0.2777(3)	0.0710(4)	0.8046(5)	0.023(2)	0.036(2)	0.045(2)	–0.004(2)	0.007(2)	–0.003(2)
C(1)	4*e*	0.1029(5)	0.0395(5)	1.2970(8)	0.040(3)	0.047(4)	0.050(3)	0.002(2)	–0.002(3)	–0.003(3)
C(2)	4*e*	0.0687(5)	–0.2175(5)	1.0204(7)	0.037(3)	0.029(3)	0.072(4)	0.001(2)	0.015(3)	0.005(3)
C(3)	4*e*	0.2858(5)	0.1642(5)	0.7003(7)	0.033(3)	0.039(3)	0.064(4)	0.003(2)	0.009(3)	0.007(3)
C(4)	4*e*	0.3956(5)	0.1968(5)	0.6221(7)	0.045(3)	0.049(4)	0.060(4)	–0.003(3)	0.015(3)	0.016(3)
C(5)	4*e*	0.5038(5)	0.1316(5)	0.6481(7)	0.032(3)	0.046(3)	0.044(3)	–0.009(2)	0.004(2)	–0.003(2)
C(6)	4*e*	0.6264(5)	0.1634(6)	0.5683(8)	0.042(3)	0.071(4)	0.069(4)	–0.017(3)	0.019(3)	0.001(3)
C(7)	4*e*	0.4952(5)	0.0364(5)	0.7542(7)	0.026(2)	0.057(4)	0.056(4)	0.007(2)	0.008(2)	0.008(3)
C(8)	4*e*	0.3820(5)	0.0084(5)	0.8285(7)	0.035(3)	0.043(3)	0.050(3)	0.004(2)	0.005(2)	0.009(2)

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