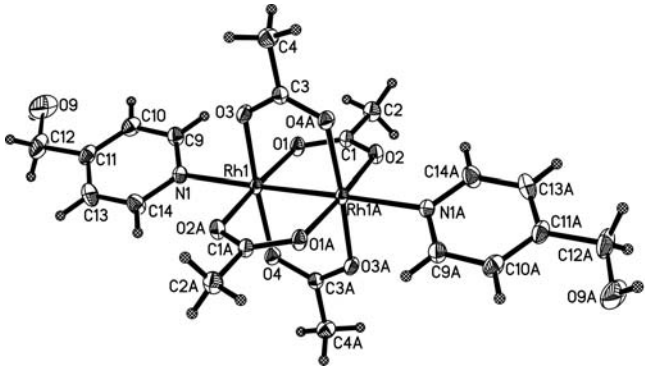
Crystal structure of tetrakis(acetato)bis(4-pyridinemethanol)dirhodium, $Rh_2(C_2H_3O_2)_4(C_6H_7NO)_2$

Qing-Song Ye[I], Jia-Lin Chen[I], Ming-Jin Xie[II], Wei-Ping Liu[*,I] and Shui-Yan Yang[I]

[I] State Key Lab of Advanced Technologies for Platinum Metals, Kunming Institute of Precious Metal, Kunming 650106, P. R. China
[II] Yunnan University, Department of Chemistry, Kunming 650031, P. R. China

Received January 24, 2011, accepted and available on-line February 2, 2011; CCDC no. 1267/3378



Abstract

$C_{20}H_{26}N_2O_{10}Rh_2$, triclinic, $P\bar{1}$ (no. 2), a = 7.275(1) Å, b = 8.237(1) Å, c = 10.757(2) Å, α = 91.873(2)°, β = 98.024(2)°, γ = 115.057(2)°, V = 575.2 Å^3, Z = 1, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.090, T = 293 K.

Source of material

$Rh_2(O_2CCH_3)_4(H_2O)_2$ (20 mg, 0.042 mmol) was dissolved in 5 ml of methanol. The solution was layered with a methanol solution of 4-pyridinemethanol (11 mg, 0.10 mmol) at room temperature. This resulted in deposition of a few pink block-shaped crystals of the title complex in a week.

Experimental details

The H atoms were positioned geometrically with d(C—H) = 0.93 - 0.97 Å, d(O—H) = 0.82 Å, and U_{iso}(H) = 1.5 U_{eq}(C,O).

Discussion

Rhodium(II) carboxylates of type $Rh_2(O_2CR)_4L_2$, in which L represents a Lewis base and R an organic group, have been attracting much attention in recent years due to their potential applications as catalysts [1,2], antitumor agents [3,4] and building blocks for supramolecular arrays [5,6]. Rhodium(II) carboxylates readily form adducts in which the axial sites are occupied by donor solvents or ligands, which has led to the isolation of a large number of adducts [6,7]. Nitrogen donor adducts of rhodium(II) carboxylates constitute the largest class of the adducts [6,7]. However, the adducts of rhodium(II) carboxylates with pyridine derivatives are relatively less reported.

In the title complex, the Rh atom is coordinated in a distorted octahedral manner. Each Rh atom is bound by four O atoms of the acetates in the equatorial coordination plane, while the other two sites are occupied by one N atom of the 4-pyridinemethanol ligand and a second metal ion. The Rh—Rh bond length is 2.4030(7) Å with the axial pyridine N atoms coordinates Rh at distance of 2.243(3) Å. The range of Rh—O distances extends from 2.035(3) to 2.057(3) Å. The Rh–Rh–O angles have a mean value of 87.79(8)°, individual angles being in the range from 87.19(9)° to 88.26(9)°. The four carboxylate oxygen atoms about Rh atom define a square plane from which the Rh atom is displaced by 0.0789(4) Å toward the axial nitrogen atom. The axial Rh–Rh–N angle is close to linear with value of 178.3(1)°. The pyridine rings in the 4-pyridinemethanol are planar with deviations not greater than 0.010 Å.

The molecular structure of the title complex is very similar to that of $Rh_2(O_2CCH_3)_4(py)_2$ [8]. However, compared to $Rh_2(O_2CCH_3)_4(py)_2$, not only the Rh—Rh bond lengths in the title complex slightly increase from 2.3963(2) to 2.4030(7) Å, but the Rh—N distances also increase by 0.016 Å, which is opposite to that expected for *trans*-effect influences in respect to the Rh—Rh bond.

The pyridyl rings in the title complex are parallel to each other with a distance of 3.615 Å between the nearest neighbors, and the distance between their centroids is 4.103 Å, which indicates π-π packing interactions [9]. The crystal packing of the title complex is further stabilized by hydrogen bonds formed between O atoms of 4-pyridinemethanol and that of the acetates with d(O···O) of 2.881(3) Å.

Table 1. Data collection and handling.

Crystal:	pink block, size 0.12 × 0.17 × 0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.93 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	56.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4110, 2406
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2048
$N(param)_{refined}$:	157
Programs:	SHELXS-97, SHELXL-97 [10]

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

Atom	Site	x	y	z	U_{iso}
H(9)	2*i*	–0.5423	0.7916	–0.1379	0.129
H(2A)	2*i*	0.4622	1.5165	0.6159	0.057
H(2B)	2*i*	0.3164	1.3861	0.6998	0.057
H(2C)	2*i*	0.2303	1.3958	0.5597	0.057
H(4A)	2*i*	–0.0404	0.6862	0.6952	0.057
H(4B)	2*i*	0.1202	0.6235	0.7627	0.057
H(4C)	2*i*	–0.0114	0.5269	0.6310	0.057

* Correspondence author (e-mail: liuweiping0917@126.com)

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(9A)	2*i*	–0.0295	0.9940	0.2993	0.043
H(10)	2*i*	–0.2933	0.9055	0.1311	0.048
H(12A)	2*i*	–0.3020	0.7428	–0.1612	0.071
H(12B)	2*i*	–0.4175	0.5670	–0.0979	0.071
H(13)	2*i*	–0.0210	0.6507	–0.0367	0.057
H(14)	2*i*	0.2404	0.7535	0.1315	0.050

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*	0.37417(5)	0.96201(4)	0.40563(3)	0.0218(2)	0.0242(2)	0.0208(2)	0.0105(1)	–0.0031(1)	–0.0010(1)
O(1)	2*i*	0.3079(5)	1.1648(4)	0.4682(3)	0.030(2)	0.031(2)	0.032(2)	0.017(1)	–0.006(1)	–0.005(1)
O(2)	2*i*	0.5419(5)	1.2343(4)	0.6456(3)	0.034(2)	0.033(2)	0.030(2)	0.019(1)	–0.004(1)	–0.006(1)
O(3)	2*i*	0.1684(4)	0.7869(4)	0.5036(3)	0.025(2)	0.032(2)	0.028(2)	0.006(1)	–0.002(1)	0.002(1)
O(4)	2*i*	0.6001(5)	1.1422(4)	0.3188(3)	0.027(2)	0.036(2)	0.026(2)	0.012(1)	–0.002(1)	0.004(1)
O(9)	2*i*	–0.5149(7)	0.7500(8)	–0.0735(4)	0.045(3)	0.149(5)	0.052(3)	0.035(3)	–0.010(2)	0.027(3)
N(1)	2*i*	0.1323(6)	0.8855(5)	0.2325(3)	0.026(2)	0.032(2)	0.023(2)	0.012(2)	–0.000(2)	0.000(2)
C(1)	2*i*	0.4021(7)	1.2557(5)	0.5734(4)	0.027(2)	0.027(2)	0.026(2)	0.010(2)	–0.001(2)	–0.002(2)
C(2)	2*i*	0.3479(8)	1.4015(6)	0.6160(4)	0.041(3)	0.034(3)	0.042(3)	0.022(2)	0.001(2)	–0.002(2)
C(3)	2*i*	0.2201(7)	0.7714(6)	0.6180(4)	0.027(2)	0.031(2)	0.028(2)	0.018(2)	–0.000(2)	–0.001(2)
C(4)	2*i*	0.0575(7)	0.6403(6)	0.6825(4)	0.036(3)	0.038(3)	0.039(3)	0.015(2)	0.007(2)	0.008(2)
C(9)	2*i*	–0.0263(7)	0.9256(6)	0.2299(4)	0.037(3)	0.038(3)	0.033(2)	0.018(2)	0.000(2)	–0.002(2)
C(10)	2*i*	–0.1872(8)	0.8712(6)	0.1293(4)	0.031(3)	0.046(3)	0.042(3)	0.018(2)	–0.002(2)	0.009(2)
C(11)	2*i*	–0.1894(8)	0.7662(7)	0.0267(4)	0.032(3)	0.040(3)	0.031(3)	0.003(2)	–0.004(2)	0.010(2)
C(12)	2*i*	–0.3592(9)	0.6975(8)	–0.0864(5)	0.046(4)	0.065(4)	0.039(3)	0.007(3)	–0.017(3)	0.009(3)
C(13)	2*i*	–0.0253(9)	0.7223(7)	0.0304(4)	0.062(4)	0.050(3)	0.027(3)	0.023(3)	–0.001(2)	–0.004(2)
C(14)	2*i*	0.1309(8)	0.7836(7)	0.1320(4)	0.044(3)	0.056(3)	0.031(3)	0.031(3)	–0.001(2)	–0.002(2)

Acknowledgment. This work was financially supported by Science and Technology Development Program of Yunnan Province, P. R. China (grant nos. 2008IA008, 2008CF002, 2009CD133).

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