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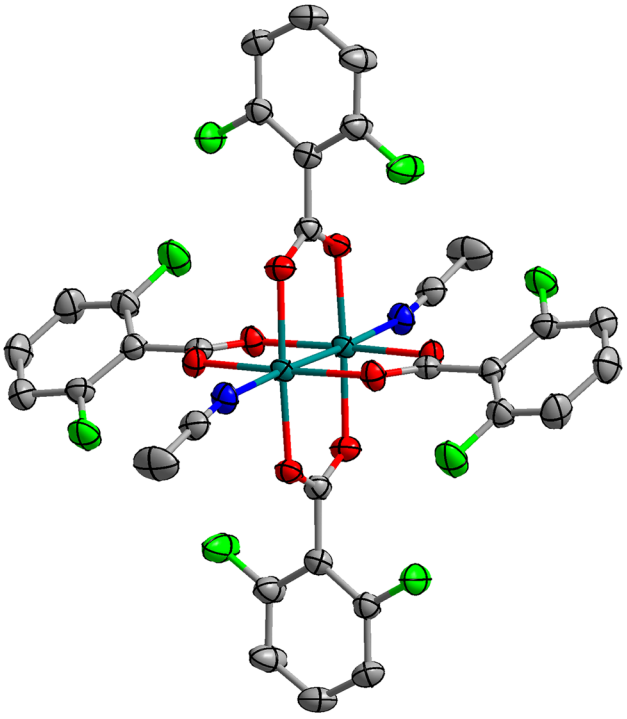
The crystal structure of bis(acetonitrile-κ^{1}N) tetrakis(μ$_2$-2,6-difluorobenzoato-κ^{2}O:O′) rhodium(II) (Rh–Rh), $C_{32}H_{18}F_8O_8N_2Rh_2$



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Abstract

$C_{32}H_{18}F_8O_8N_2Rh_2$, monoclinic, $P2_1/n$ (no. 11), a = 9.28200(12) Å, b = 11.33638(13) Å, c = 16.0352(2) Å, β = 105.9326(14)° V = 1622.47 Å^3, Z = 4, $R_{gt}(F)$ = 0.0297, $wR_{ref}(F^2)$ = 0.0763, T = 150 K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Blue-green plate
Size:	0.10 × 0.05 × 0.02 mm
Wavelength:	Cu *K*α radiation (1.54184 Å)
μ:	9.152 mm^{-1}
Diffractometer, scan mode:	Rigaku, XtaLAB, φ and ω scans
θ_{max}, completeness:	74.12°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8299, 3177, 0.0268
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$,
$N(param)_{refined}$:	236
Programs:	CrysAlis^{PRO} [1], SHELX [2], Olex2 [3], Diamond [4]

1 Source of material

Rhodium(II) acetate was prepared by a method described in the literature [5]. $Rh_2(2,6–2F–C_6H_3C_OO)_4{\cdot}2CH_3C_N$ was prepared by a ligand-exchange reaction of rhodium(II) acetate with 2,6-difluorobenzoic acid. A solution of rhodium(II) acetate (0.100 g, 0.226 mmol), 2,6-difluoronitrobenzoic acid (3.214 g, 0.0164 mol) in 5 mL of diethyleneglycoldimethylether was stirred for 6 h at 190 °C. After evaporation of the solvent, recrystallization from acetonitrile gave blue-green plate crystals, yield 68.5 %.

2 Experimental details

Coordinates of hydrogen atoms were not refined. Their U_{iso} values were set to 1.2 U_{eq} of the parent atoms.

3 Comment

Dirhodium tetracarboxylates have significant potential for catalysis, molecular devices as well as pharmaceutical chemistry [6–8]. This type of paddlewheel complexes such as *cis*-$[Rh_2(xhp)_2(CH_3CN)_n][BF_4]_2$ (n = 5 or 6) and $[Rh_2$(guaiazulene carboxylate$)_4(H_2O)_2]$ may have fluorescent properties [9–11].

In the crystal structure of the title molecule, two rhodium(II) ions are bridged by four 2,6-difluorobenzoato

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5426 (4)	1.0594 (3)	−0.1484 (2)	0.0270 (6)
C2	0.5700 (3)	1.0964 (3)	−0.2324 (2)	0.0285 (6)
C3	0.5086 (4)	1.1980 (3)	−0.2761 (2)	0.0323 (7)
C4	0.5446 (4)	1.2416 (3)	−0.3480 (2)	0.0380 (8)
H4	0.4995 (4)	1.3097 (3)	−0.3756 (2)	0.0456 (9)*
C5	0.6494 (5)	1.1812 (4)	−0.3778 (2)	0.0450 (9)
H5	0.6783 (5)	1.2104 (4)	−0.4250 (2)	0.0540 (11)*
C6	0.7121 (5)	1.0779 (4)	−0.3384 (2)	0.0454 (9)
H6	0.7807 (5)	1.0362 (4)	−0.3597 (2)	0.0544 (11)*
C7	0.6715 (4)	1.0380 (3)	−0.2677 (2)	0.0364 (8)
C8	0.4234 (3)	0.7888 (3)	−0.0579 (2)	0.0271 (6)
C9	0.3789 (3)	0.6659 (3)	−0.0883 (2)	0.0286 (6)
C10	0.3850 (4)	0.6244 (3)	−0.1686 (2)	0.0311 (7)
C11	0.3441 (4)	0.5122 (3)	−0.1975 (2)	0.0374 (8)
H11	0.3484 (4)	0.4876 (3)	−0.2521 (2)	0.0449 (9)*
C12	0.2962 (4)	0.4367 (3)	−0.1426 (3)	0.0435 (9)
H12	0.2693 (4)	0.3597 (3)	−0.1604 (3)	0.0522 (10)*
C13	0.2875 (5)	0.4731 (3)	−0.0625 (3)	0.0469 (10)
H13	0.2542 (5)	0.4222 (3)	−0.0263 (3)	0.0563 (12)*
C14	0.3293 (4)	0.5869 (3)	−0.0371 (2)	0.0396 (8)
C15	0.9636 (4)	0.8445 (3)	0.0894 (2)	0.0344 (7)
C16	1.0944 (4)	0.7667 (4)	0.1125 (3)	0.0596 (12)
H16a	1.1723 (14)	0.7989 (16)	0.0905 (19)	0.0895 (19)*
H16b	1.130 (2)	0.760 (2)	0.1745 (4)	0.0895 (19)*
H16c	1.067 (1)	0.6901 (9)	0.0877 (19)	0.0895 (19)*
F1	0.7334 (3)	0.9364 (2)	−0.2306 (2)	0.0552 (6)
F2	0.4330 (3)	0.7010 (2)	−0.2201 (1)	0.0465 (5)
F3	0.3250 (3)	0.6247 (2)	0.0424 (2)	0.0590 (7)
F4	0.4113 (3)	1.2603 (2)	−0.2452 (1)	0.0463 (5)
N1	0.8620 (3)	0.9017 (3)	0.0702 (2)	0.0320 (6)
O1	0.5605 (2)	0.8055 (2)	−0.0232 (1)	0.0283 (5)
O2	0.6541 (2)	1.0186 (2)	−0.0920 (1)	0.0299 (5)
O3	0.6816 (2)	1.1369 (2)	0.0692 (2)	0.0309 (5)
O4	0.5876 (2)	0.9259 (2)	0.1402 (1)	0.0301 (5)
Rh1	0.6283 (1)	0.9692 (1)	0.0251 (1)	0.02365 (9)

ligands to form a paddle-wheel dimer. The Rh1–Rh1a distance is 2.399(1) Å, which is slightly shorter than that of adduct complexes of rhodium(II) benzoate (2.405(1) Å, for $[Rh_2(O_2CC_6H_5)_4(DMSO)_2]\cdot C_6H_5CH_3$ [9], 2.402(1) Å, for $[Rh_2(O_2CC_6H_5)_4(py)_2]$ [10]. But this bond length is still in the range for tetracarboxylato dirhodium(II) dimers (2.35–2.45 Å,) [12]. Thus two rhodium(II) ions reported here are assigned to be singly bonded.

The coordination geometries around the rhodium(II) ions are square-bipyramidal, which has been well established before [11–20]. The axial positions of the dimer core are occupied by nitrogen atoms of the acetonitrile molecules with Rh–N distances of 2.225 Å, which is slightly shorter than those reported in the literature (c.a. 0.012 Å and 0.008 Å) [6, 13]. The tightly binding of axial base reported here may be due to the two fluorine atom 2,6-difluoronitrobenzoic cation, which make the electron density of $[Rh_2]$ unit lower than similar compounds [6, 13] and enhance its Lewis acidity at axial position.

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