Crystal structure of bis(acetylacetonato-κ^2O,O')-(diacetylmethanido-κC)-(3-pyridylmethanol)iridium(III), $Ir(C_5H_7O_2)_3(C_6H_7NO)$

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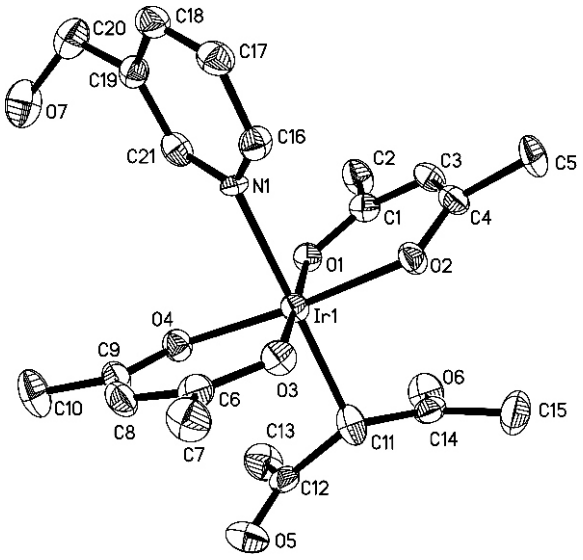

Abstract

$C_{21}H_{28}IrNO_7$, monoclinic, *C*1*c*1 (no. 9), a = 16.938(2) Å, b = 8.0768(8) Å, c = 16.265(2) Å, β = 95.124(1)°, V = 2216.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.028, $wR_{ref}(F^2)$ = 0.053, T = 298 K.

Source of material

The titled complex was prepared by refluxing aquabis(acetylacetonato-κ^2O,O')(diacetylmethanido-κC)iridium(III) and a large excess of 3-pyridylmethanol, and then the insoluble residual was filtered off. The filtrate was slowly cooled to room temperature along with evaporation, a yellow crystalline product precipitated. Single crystals were selected from the product for the X-ray diffraction analysis.

Experimental details

All the hydrogen atoms were positioned geometrically with d(C—H) = 0.93 - 0.98 Å, d(O—H) = 0.82 Å and refined as riding with U_{iso}(H) = 1.2 or 1.5 U_{eq}(C) and U_{iso}(H) = 1.5 U_{eq}(O). The refined Flack parameter of 0.004(9) implies that the absolute structure is correct.

Discussion

In the title crystal structure, the Ir atom is six-coordinated and situated in a slightly distorted octahedral environment, formed by four oxygen atoms of two acetylacetone ligands, one carbon atom of one acetylacetone ligand and one N atom of 3-pyridylmethanol. The average O–Ir–O chelating angle is 95.135°. The average Ir—O bond length of two acetylacetone ligands is 2.025(4) Å, Ir—C bond length is found to be 2.09(2) Å, which agree with the literature data of $Ir(C_5H_7O_2)_3$, $Ir(C_5H_7O_2)_3(H_2O)$, $Ir(C_5H_7O_2)_3(C_2H_6SO)$ and $Ir(C_5H_7O_2)_3(CH_3CN) \cdot 1.5H_2O$ [1-5]. The Ir—N bond length is found to be 2.13(1) Å. Change in the coordination mode of one acetylacetonate ligand of tris(acetylacetonato-*O*,*O*)iridium(III) lead to the formation of the direct Ir-C bond . In this complex, the average Ir—O, Ir—C and Ir—N bond lengths are close to each other. The Ir—C bond length is found to be between a Ir—C σ-bond (2.00 - 2.02 Å) and a Ir—C π-bond (2.27 - 2.31 Å) [3]. The crystal structure also reveals that there are two different types of coordinated acac ligands: a conventional bidentate (O-bonded acac ligand) and a γ-C bonded acac ligand in the title complex, as Periana proposed [3].

The crystal packing is stablilized by extensive hydrogen bonds formed between 3-pyridinemethanol and carbonyl O atoms of the acetylacetone ligand with d(O7–H7···O6) of 2.864(8) Å and ∠O7–H7···O6 = 164.3°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.12 × 0.14 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	60.65 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	56.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7210, 3791
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3397
$N(param)_{refined}$:	278
Programs:	SHELXS-97, SHELXL-97 [6], DIAMOND [7]

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

Atom	Site	x	y	z	U_{iso}
H(7)	4*a*	0.6107	0.4127	0.2983	0.104
H(2A)	4*a*	0.2386	0.7592	0.4057	0.079
H(2B)	4*a*	0.3151	0.8082	0.4617	0.079
H(2C)	4*a*	0.3138	0.6455	0.4090	0.079
H(3)	4*a*	0.3283	1.0699	0.3974	0.048
H(5A)	4*a*	0.4258	1.3422	0.3174	0.078
H(5B)	4*a*	0.3462	1.3382	0.3596	0.078
H(5C)	4*a*	0.3455	1.3818	0.2656	0.078
H(7A)	4*a*	0.4850	1.0374	–0.0558	0.083
H(7B)	4*a*	0.5446	0.8904	–0.0622	0.083
H(7C)	4*a*	0.5622	1.0281	0.0048	0.083
H(8)	4*a*	0.5140	0.6500	0.0001	0.054

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(10A)	4*a*	0.5095	0.3714	0.1142	0.101
H(10B)	4*a*	0.4689	0.3777	0.0238	0.101
H(10C)	4*a*	0.4178	0.3436	0.0978	0.101
H(11)	4*a*	0.2857	0.9477	0.0612	0.055
H(13A)	4*a*	0.1710	0.5800	0.1095	0.095
H(13B)	4*a*	0.2489	0.5732	0.1692	0.095
H(13C)	4*a*	0.2408	0.4637	0.0893	0.095
H(15A)	4*a*	0.1623	1.1393	0.0947	0.102

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(15B)	4*a*	0.2467	1.1776	0.1381	0.102
H(15C)	4*a*	0.1740	1.1607	0.1908	0.102
H(16)	4*a*	0.5312	1.0789	0.2137	0.047
H(17)	4*a*	0.6525	1.0814	0.2877	0.055
H(18)	4*a*	0.6928	0.8524	0.3670	0.054
H(20A)	4*a*	0.6759	0.5627	0.3949	0.073
H(20B)	4*a*	0.5966	0.5692	0.4375	0.073
H(21)	4*a*	0.4891	0.6410	0.2923	0.048

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}
Ir(1)	4*a*	0.38668(3)	0.86191(2)	0.17848(3)	0.0385(1)	0.0298(1)	0.0291(1)	–0.0001(3)	0.00554(7)	0.0010(3)
N(1)	4*a*	0.4998(7)	0.859(1)	0.2476(6)	0.025(4)	0.038(5)	0.025(5)	0.004(3)	–0.009(3)	–0.004(3)
O(1)	4*a*	0.3397(3)	0.7651(5)	0.2778(3)	0.040(3)	0.036(3)	0.030(3)	0.002(2)	0.007(2)	0.004(2)
O(2)	4*a*	0.3767(3)	1.1003(5)	0.2149(3)	0.055(3)	0.025(2)	0.035(2)	0.001(2)	0.003(2)	–0.003(2)
O(3)	4*a*	0.4391(3)	0.9613(5)	0.0830(3)	0.046(3)	0.038(3)	0.037(3)	–0.004(2)	0.009(2)	0.006(2)
O(4)	4*a*	0.4061(3)	0.6230(5)	0.1473(3)	0.046(3)	0.033(3)	0.040(3)	0.001(2)	0.006(2)	0.001(2)
O(5)	4*a*	0.2791(3)	0.6804(7)	–0.0046(3)	0.079(4)	0.080(4)	0.036(3)	–0.002(3)	0.001(3)	–0.008(3)
O(6)	4*a*	0.1755(3)	0.8587(6)	0.1999(3)	0.053(3)	0.066(4)	0.063(4)	–0.002(3)	0.024(3)	0.000(3)
O(7)	4*a*	0.5934(3)	0.4161(7)	0.3437(4)	0.072(4)	0.043(3)	0.095(5)	0.003(3)	0.020(3)	0.017(3)
C(1)	4*a*	0.3258(5)	0.8551(9)	0.3383(5)	0.037(5)	0.042(4)	0.034(5)	–0.003(4)	0.006(4)	0.002(4)
C(2)	4*a*	0.2955(5)	0.7579(9)	0.4105(5)	0.076(6)	0.045(5)	0.041(4)	0.003(4)	0.022(4)	0.003(4)
C(3)	4*a*	0.3374(4)	1.0254(8)	0.3463(4)	0.048(4)	0.045(4)	0.028(4)	–0.002(3)	0.009(3)	–0.009(3)
C(4)	4*a*	0.3606(4)	1.1377(8)	0.2884(4)	0.040(4)	0.041(4)	0.034(4)	–0.002(3)	0.005(3)	–0.011(3)
C(5)	4*a*	0.3704(5)	1.3157(8)	0.3096(5)	0.072(6)	0.023(4)	0.062(5)	0.002(3)	0.013(4)	–0.008(3)
C(6)	4*a*	0.4772(5)	0.865(1)	0.0351(6)	0.035(5)	0.058(6)	0.037(5)	0.002(4)	0.008(4)	0.002(4)
C(7)	4*a*	0.5213(4)	0.964(1)	–0.0250(5)	0.053(5)	0.066(5)	0.050(5)	–0.007(4)	0.018(4)	0.001(4)
C(8)	4*a*	0.4828(4)	0.6970(9)	0.0382(4)	0.049(4)	0.050(5)	0.038(4)	0.003(3)	0.012(3)	–0.012(3)
C(9)	4*a*	0.4490(4)	0.5855(9)	0.0893(4)	0.044(4)	0.042(4)	0.043(4)	0.004(3)	0.008(3)	–0.012(3)
C(10)	4*a*	0.4625(6)	0.4031(9)	0.0805(6)	0.094(7)	0.038(5)	0.075(6)	0.006(4)	0.032(5)	–0.008(4)
C(11)	4*a*	0.279(1)	0.870(1)	0.106(1)	0.048(8)	0.035(7)	0.058(8)	–0.005(5)	0.025(6)	–0.005(5)
C(12)	4*a*	0.2611(6)	0.702(2)	0.0664(7)	0.027(4)	0.043(6)	0.040(5)	0.000(4)	–0.007(4)	0.000(4)
C(13)	4*a*	0.2276(5)	0.568(1)	0.1126(5)	0.073(6)	0.049(5)	0.068(6)	–0.014(4)	0.005(4)	–0.002(4)
C(14)	4*a*	0.2133(4)	0.941(1)	0.1526(5)	0.035(4)	0.054(5)	0.039(4)	0.004(3)	–0.007(3)	0.000(4)
C(15)	4*a*	0.1977(5)	1.1204(9)	0.1432(6)	0.070(6)	0.050(5)	0.085(7)	0.022(4)	0.004(5)	0.005(5)
C(16)	4*a*	0.5474(4)	0.9875(9)	0.2456(5)	0.044(4)	0.030(4)	0.043(5)	0.000(3)	0.001(4)	0.007(3)
C(17)	4*a*	0.6197(4)	0.9893(9)	0.2893(4)	0.045(4)	0.044(4)	0.048(4)	–0.009(3)	0.004(3)	–0.007(3)
C(18)	4*a*	0.6439(4)	0.8528(9)	0.3361(4)	0.038(4)	0.058(5)	0.040(4)	0.000(4)	0.005(3)	–0.011(4)
C(19)	4*a*	0.5946(4)	0.7174(8)	0.3363(4)	0.040(4)	0.041(4)	0.036(4)	0.006(3)	0.007(3)	0.004(3)
C(20)	4*a*	0.6186(5)	0.565(1)	0.3845(5)	0.055(5)	0.063(5)	0.064(6)	0.011(4)	0.006(4)	0.013(5)
C(21)	4*a*	0.5236(6)	0.731(2)	0.2916(7)	0.046(6)	0.032(5)	0.043(5)	–0.008(5)	0.012(5)	–0.004(4)

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References

1. Isakova, V. G.; Baidina, I. A.; Morozova, N. B.; Igumenov, I. K.: γ-Halogenated iridium(III)acetylacetonates. Polyhedron **19** (2000) 1097-1103.
2. Chang, Q. W.; Xie, M. J.; Liu, W. P.; Chen, X. Z.; Ye, Q. S.: Bis-(acetylacetonato-2*O*,*O'*)aqua(diacetylmethanido-*C*)iridium(III). Acta Crystallogr. **E65** (2009) m1264.
3. Matsumoto, T.; Periana, R. A.; Taube, D. J.; Yoshida, H.: Regioselective hydrophenylation of olefins catalyzed by an Ir(III) complex. J. Mol. Catal. **A180** (2002) 1-18.
4. Jiang, J.; Xie, M. J.; Chang, Q. W.; Chen, J. L.; Xie, X. T.; Ye, Q. S.; Chen, X. Z.; Yu, Y.; Liu, W. P.: Crystal structure of bis(acetylacetonato-κ^2*O*,*O'*)-(diacetylmethanido-κ*C*)-(dimethylsulfoxide-*S*)iridium(III), $Ir(C_5H_7O_2)_3(C_2H_6SO)$. Z. Kristallogr. NCS **225** (2010) 575-576.
5. Chang, Q. W.; Hu, C, Y.; Pan, Z. F.; Chen, J. L.; Ye, Q. S.; Chen, X. Z.; Yu, Y.; Liu, W. P.: Crystal structure of bis(acetylacetonato-κ^2*O*,*O'*)-(diacetylmethanido-κ*C*)-(acetonitrile-*N*)iridium(III) sesquihydrate, $Ir(C_5H_7O_2)_3(CH_3CN) \cdot 1.5H_2O$. Z. Kristallogr. NCS **225** (2010) 667-668.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
7. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.2c. Crystal Impact, Bonn, Germany 1998.