Crystal structure of bis(acetylacetonato-κ^2O,O')-(diacetylmethanido-κC)-(piperidine)iridium(III), $Ir(C_5H_7O_2)_3(C_5H_{11}N)$

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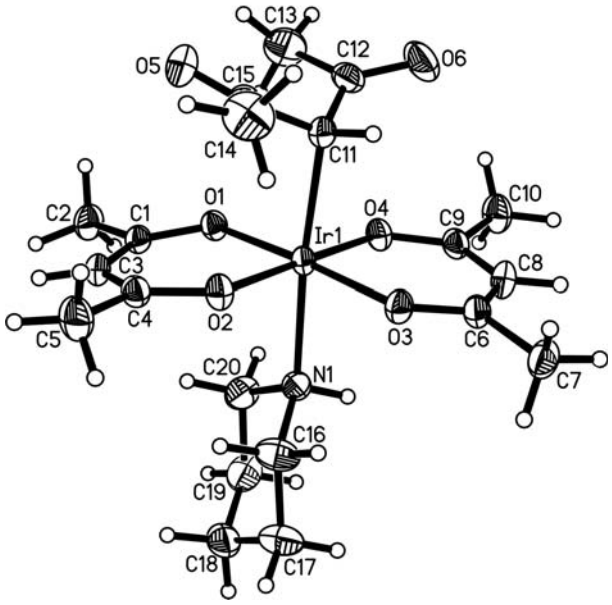

Abstract

$C_{20}H_{32}IrNO_6$, monoclinic, $P2_1/n$ (no. 14), a = 11.1059(8) Å, b = 14.477(1) Å, c = 13.735(1) Å, β = 94.384(1)°, V = 2201.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.026, $wR_{ref}(F^2)$ = 0.059, T = 298 K.

Source of material

The title complex was prepared by refluxing aquabis(acetylacetonato-κ^2O,O')-(diacetylmethanido-κC)iridium(III) and a large excess of piperidine, 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

The H atoms were positioned geometrically with d(C—H) = 0.93 - 0.98 Å, d(N—H) = 0.91 Å and refined as riding with U_{iso}(H) = 1.2 U_{eq}(C) or U_{iso}(H) = 1.5 U_{eq}(C_{methyl},N).

Discussion

The Ir atom is six-coordinated and situated in a slightly distorted octahedral environment, formed by four oxygen atoms of two acetyacetone ligands, one carbon atom of one acetylacetone ligand and one N atom of piperidine. The average O–Ir–O chelating angle is 94.53°. The average d(Ir—O) is 2.02 Å and d(Ir—C) is 2.158 Å, which agree with the literature data of $Ir(C_5H_7O_2)_3$, $Ir(C_5H_7O_2)_3(H_2O)$ and $Ir(C_5H_7O_2)_3(C_2H_6SO)$ [1-5]. Ir—N bond length is found to be 2.176 Å. Change in the coordination mode of one acetylacetonate ligand of tris(acetyacetonato-O,O)iridium(III) lead to the formation of the direct Ir—C bond. In this type complex, Ir—C bond lengths are close to each other, found to be between Ir—C σ-bond (2.00 - 2.02 Å) and Ir—C π-bond (2.27 - 3.31 Å) [3]. The crystal packing of the title complex is stablilized by extensive hydrogen bonds formed between piperidine and carbonyl O atoms of the acetylacetone ligand with d(N1–H1···O5) = 3.321(5) Å and ∠N1–H1···O5 = 158.2°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.12 × 0.19 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	60.98 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	56.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14756, 5206
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4234
$N(param)_{refined}$:	259
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(1)	4*e*	0.1356	0.2298	0.5381	0.046
H(2A)	4*e*	0.2745	0.4283	0.9083	0.078
H(2B)	4*e*	0.1570	0.3770	0.9347	0.078
H(2C)	4*e*	0.1577	0.4327	0.8368	0.078
H(3)	4*e*	0.1932	0.2229	0.9324	0.047
H(5A)	4*e*	0.2025	0.0070	0.8624	0.088
H(5B)	4*e*	0.2127	0.0680	0.9570	0.088
H(5C)	4*e*	0.3294	0.0273	0.9160	0.088
H(7A)	4*e*	0.4369	0.0142	0.4313	0.082
H(7B)	4*e*	0.3840	0.0718	0.3412	0.082
H(7C)	4*e*	0.2968	0.0209	0.4079	0.082
H(8)	4*e*	0.3981	0.2255	0.3637	0.057
H(10A)	4*e*	0.3274	0.4340	0.4081	0.086
H(10B)	4*e*	0.4221	0.3789	0.3521	0.086
H(10C)	4*e*	0.4631	0.4310	0.4490	0.086
H(11)	4*e*	0.5551	0.1834	0.6538	0.049
H(13A)	4*e*	0.5954	0.4531	0.7189	0.109
H(13B)	4*e*	0.5910	0.3844	0.8067	0.109
H(13C)	4*e*	0.4713	0.4134	0.7467	0.109
H(15A)	4*e*	0.5703	0.0709	0.8742	0.117
H(15B)	4*e*	0.6476	0.0763	0.7835	0.117
H(15C)	4*e*	0.5088	0.0554	0.7689	0.117
H(16A)	4*e*	0.0809	0.1129	0.6832	0.073
H(16B)	4*e*	0.1303	0.0811	0.5848	0.073

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(17A)	4*e*	–0.0787	0.0594	0.5800	0.081
H(17B)	4*e*	–0.0468	0.1295	0.4984	0.081
H(18A)	4*e*	–0.2051	0.1907	0.5804	0.081
H(18B)	4*e*	–0.1291	0.1807	0.6811	0.081

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(19A)	4*e*	–0.1182	0.3335	0.6300	0.078
H(19B)	4*e*	–0.0725	0.3022	0.5298	0.078
H(20A)	4*e*	0.0922	0.3515	0.6305	0.066
H(20B)	4*e*	0.0590	0.2834	0.7130	0.066

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*e*	0.32671(1)	0.224138(9)	0.656806(9)	0.03515(8)	0.03240(8)	0.02760(8)	0.00065(6)	0.00791(6)	–0.00063(6)
N(1)	4*e*	0.1372(3)	0.2192(2)	0.6035(2)	0.037(2)	0.040(2)	0.037(2)	0.001(1)	0.002(1)	0.002(1)
O(1)	4*e*	0.2900(2)	0.3257(2)	0.7503(2)	0.041(1)	0.036(1)	0.037(1)	–0.000(1)	0.010(1)	–0.003(1)
O(2)	4*e*	0.3027(2)	0.1216(2)	0.7535(2)	0.050(2)	0.035(1)	0.035(1)	0.002(1)	0.011(1)	0.002(1)
O(3)	4*e*	0.3531(2)	0.1215(2)	0.5605(2)	0.047(2)	0.036(1)	0.034(1)	0.001(1)	0.008(1)	–0.004(1)
O(4)	4*e*	0.3465(2)	0.3270(2)	0.5602(2)	0.046(1)	0.038(1)	0.035(1)	0.000(1)	0.011(1)	0.005(1)
O(5)	4*e*	0.5492(3)	0.2382(2)	0.8713(2)	0.076(2)	0.080(2)	0.037(2)	–0.003(2)	0.006(2)	–0.003(2)
O(6)	4*e*	0.6189(3)	0.3322(3)	0.6003(2)	0.058(2)	0.126(3)	0.062(2)	–0.014(2)	0.023(2)	0.025(2)
C(1)	4*e*	0.2450(3)	0.3089(3)	0.8309(3)	0.034(2)	0.042(2)	0.031(2)	0.002(2)	0.004(2)	–0.004(2)
C(2)	4*e*	0.2049(4)	0.3945(3)	0.8824(3)	0.061(3)	0.051(2)	0.046(2)	0.005(2)	0.012(2)	–0.013(2)
C(3)	4*e*	0.2293(3)	0.2232(2)	0.8735(3)	0.042(2)	0.046(2)	0.029(2)	–0.001(2)	0.008(2)	–0.003(2)
C(4)	4*e*	0.2617(3)	0.1373(2)	0.8374(3)	0.039(2)	0.040(2)	0.035(2)	–0.001(2)	0.005(2)	0.004(2)
C(5)	4*e*	0.2506(4)	0.0522(3)	0.8988(3)	0.078(3)	0.049(2)	0.050(3)	–0.002(2)	0.016(2)	0.014(2)
C(6)	4*e*	0.3685(3)	0.1384(3)	0.4706(3)	0.041(2)	0.048(2)	0.034(2)	0.002(2)	0.009(2)	–0.003(2)
C(7)	4*e*	0.3719(4)	0.0536(3)	0.4070(3)	0.067(3)	0.055(2)	0.043(2)	–0.002(2)	0.010(2)	–0.014(2)
C(8)	4*e*	0.3817(4)	0.2250(3)	0.4291(3)	0.059(3)	0.055(2)	0.029(2)	0.004(2)	0.010(2)	–0.004(2)
C(9)	4*e*	0.3736(3)	0.3109(3)	0.4733(3)	0.039(2)	0.050(2)	0.033(2)	0.000(2)	0.006(2)	0.007(2)
C(10)	4*e*	0.3988(4)	0.3965(3)	0.4154(3)	0.076(3)	0.054(3)	0.044(2)	–0.001(2)	0.016(2)	0.011(2)
C(11)	4*e*	0.5183(3)	0.2272(3)	0.6971(3)	0.038(2)	0.050(2)	0.035(2)	0.001(2)	0.006(2)	–0.008(2)
C(12)	4*e*	0.5688(3)	0.3202(3)	0.6751(3)	0.033(2)	0.081(3)	0.045(2)	–0.004(2)	0.002(2)	0.014(2)
C(13)	4*e*	0.5554(4)	0.3999(3)	0.7429(4)	0.081(3)	0.053(3)	0.084(4)	–0.023(3)	0.008(3)	0.001(3)
C(14)	4*e*	0.5444(3)	0.1912(3)	0.7983(3)	0.041(2)	0.053(2)	0.046(2)	0.003(2)	0.006(2)	0.000(2)
C(15)	4*e*	0.5701(4)	0.0892(3)	0.8070(4)	0.072(3)	0.066(3)	0.096(4)	0.021(3)	0.002(3)	0.014(3)
C(16)	4*e*	0.0811(4)	0.1272(3)	0.6142(4)	0.050(2)	0.044(2)	0.087(3)	–0.007(2)	0.000(2)	0.009(2)
C(17)	4*e*	–0.0464(4)	0.1203(3)	0.5684(4)	0.052(3)	0.061(3)	0.088(4)	–0.017(2)	–0.004(3)	0.007(3)
C(18)	4*e*	–0.1241(4)	0.1930(4)	0.6121(3)	0.042(2)	0.109(4)	0.050(3)	–0.007(3)	–0.001(2)	0.011(3)
C(19)	4*e*	–0.0704(4)	0.2876(3)	0.5988(4)	0.049(3)	0.085(3)	0.060(3)	0.020(2)	–0.003(2)	–0.011(3)
C(20)	4*e*	0.0587(4)	0.2911(3)	0.6428(3)	0.048(2)	0.059(3)	0.057(3)	0.010(2)	–0.001(2)	–0.012(2)

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