Crystal structure of bis[2-(2-naphthyl)-4,6-dimethylpyrimidinyl-κ^2C,N](dibenzoylmethanato)iridium(III) — *n*-hexane (1:1), $[Ir(C_{16}H_{13}N_2)_2(C_{15}H_{11}O_2)] \cdot C_6H_{14}$

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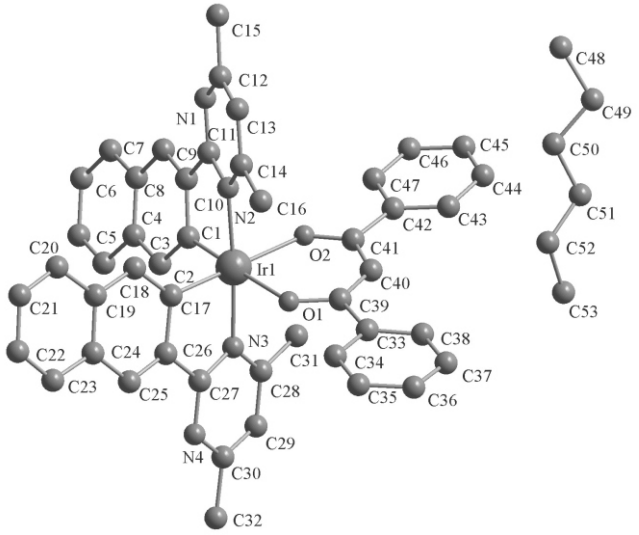

Abstract

$C_{53}H_{51}IrN_4O_2$, triclinic, $P\bar{1}$ (no. 2), a = 11.0757(9) Å, b = 13.423(1) Å, c = 17.156(2) Å, α = 90.282(1)°, β = 105.346(1)°, γ = 112.146(1)°, V = 2262.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.041, $wR_{ref}(F^2)$ = 0.090, T = 296 K.

Source of material

The title compound was prepared as described in literature [1], using dibenzoylmethane instead of acetylacetonate, and recrystallized from dichloromethane-petroleum ether solution at room temperature to give the desired crystals suitable for single-crystal X-ray diffraction-analysis.

Discussion

Cyclometalated iridium complexes have been studied extensively for their potential application in organic light-emitting diodes (OLED) [2,3]. β-Diketonates as ancillary ligands can be an effective way to improve the properties of bis-cyclometalated Ir(III) complexes [3,4]. As is known, the Ir(III) Cl-bridged dimers were directly subjected to bridge-splitting reaction with β-diketonates to produce the mononuclear bis-cyclometalated Ir(III) diketonate complexes [5-8].

The crystal structure analysis of the title compound shows a distorted octahedral coordination of the iridium(III) center. The central iridium(III) atom is surrounded by two cyclometalating ligands and one ancillary ligand dibenzoylmethane with *cis*-C–C, *trans*-N–N and *cis*-O–O chelate dispositions. The distances d(Ir—C) and d(Ir—N) are slightly longer than those of cyclometalated Ir(III) dimers, which may be caused by the interactions between the ancillary ligand and the cyclometalating ligands. The distances d(Ir—O) are similar to the reported values of other cyclometalated iridium(III) complexes [7,8]. In the title crystal structure, there exist intermolecular C–H···N hydrogen bonds (H45···N1 = 2.617 Å, 160.5°), causing a dimeric structure.

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Table 1. Data collection and handling.

Crystal:	red block, size 0.10 × 0.15 × 0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	29.95 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX-II CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17021, 8388
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6163
$N(param)_{refined}$:	547
Programs:	SHELXS-97, SHELXL-97, SHELXTL [9]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.5686	0.3224	0.1270	0.074
H(4)	2*i*	0.5502	0.1891	0.0217	0.099
H(5)	2*i*	0.4204	0.0497	–0.0768	0.118
H(6)	2*i*	0.1845	–0.0225	–0.1082	0.120
H(7)	2*i*	0.0809	0.0497	–0.0386	0.103
H(9)	2*i*	0.0986	0.1764	0.0753	0.080
H(13)	2*i*	0.1076	0.3904	0.3693	0.097
H(15A)	2*i*	–0.1537	0.2395	0.1997	0.186
H(15B)	2*i*	–0.1265	0.2897	0.2885	0.186
H(15C)	2*i*	–0.1221	0.1759	0.2735	0.186
H(16A)	2*i*	0.4607	0.5027	0.4099	0.136
H(16B)	2*i*	0.3431	0.4932	0.4477	0.136
H(16C)	2*i*	0.3808	0.5781	0.3866	0.136
H(18)	2*i*	0.4491	0.2954	0.3752	0.076
H(20)	2*i*	0.4761	0.1818	0.4873	0.110
H(21)	2*i*	0.6154	0.1295	0.5847	0.136
H(22)	2*i*	0.8461	0.2022	0.6077	0.139
H(23)	2*i*	0.9431	0.3260	0.5298	0.117
H(25)	2*i*	0.9161	0.4375	0.4142	0.083
H(29)	2*i*	0.8979	0.6407	0.1218	0.103
H(31A)	2*i*	0.5488	0.5290	0.0812	0.152
H(31B)	2*i*	0.6669	0.6043	0.0481	0.152
H(31C)	2*i*	0.6181	0.6535	0.1109	0.152
H(32A)	2*i*	1.1617	0.6298	0.2884	0.177
H(32B)	2*i*	1.1392	0.6895	0.2109	0.177

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(32C)	2*i*	1.1203	0.5678	0.2016	0.177
H(34)	2*i*	0.7511	0.7051	0.4524	0.126
H(35)	2*i*	0.8854	0.8414	0.5577	0.171
H(36)	2*i*	0.8854	1.0113	0.5473	0.164
H(37)	2*i*	0.7589	1.0478	0.4317	0.149
H(38)	2*i*	0.6233	0.9114	0.3276	0.117
H(40)	2*i*	0.4983	0.7865	0.2403	0.084
H(43)	2*i*	0.3660	0.8262	0.1529	0.096
H(44)	2*i*	0.2149	0.8627	0.0490	0.120
H(45)	2*i*	0.0784	0.7374	–0.0593	0.141
H(46)	2*i*	0.0930	0.5708	–0.0663	0.159
H(47)	2*i*	0.2397	0.5301	0.0395	0.121
H(48A)	2*i*	–0.0227	0.8780	0.3167	0.338

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(48B)	2*i*	–0.0827	0.8384	0.2232	0.338
H(48C)	2*i*	–0.1240	0.9224	0.2616	0.338
H(49A)	2*i*	0.0438	1.0079	0.1921	0.358
H(49B)	2*i*	0.0932	1.0566	0.2840	0.358
H(50A)	2*i*	0.1526	0.8888	0.2315	0.390
H(50B)	2*i*	0.2141	0.9529	0.3190	0.390
H(51A)	2*i*	0.2813	1.0248	0.1775	0.294
H(51B)	2*i*	0.3042	1.1120	0.2474	0.294
H(52A)	2*i*	0.4097	0.9529	0.2797	0.260
H(52B)	2*i*	0.4519	1.0600	0.3361	0.260
H(53A)	2*i*	0.5219	1.0427	0.1930	0.276
H(53B)	2*i*	0.6223	1.0946	0.2795	0.276
H(53C)	2*i*	0.5358	1.1549	0.2299	0.276

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}
C(1)	2*i*	0.4183(6)	0.3379(4)	0.1646(3)	0.068(4)	0.061(4)	0.049(3)	0.034(3)	0.018(3)	0.016(3)
C(2)	2*i*	0.4746(6)	0.2935(5)	0.1171(3)	0.067(4)	0.068(4)	0.053(3)	0.026(3)	0.023(3)	0.007(3)
C(3)	2*i*	0.3959(7)	0.2077(5)	0.0557(3)	0.084(4)	0.056(4)	0.058(4)	0.033(3)	0.027(3)	0.012(3)
C(4)	2*i*	0.4560(8)	0.1616(5)	0.0105(4)	0.111(5)	0.078(5)	0.071(4)	0.044(4)	0.039(4)	–0.003(4)
C(5)	2*i*	0.3786(9)	0.0788(6)	–0.0481(5)	0.127(7)	0.088(5)	0.099(6)	0.047(5)	0.059(5)	–0.001(5)
C(6)	2*i*	0.2365(9)	0.0349(6)	–0.0673(4)	0.130(7)	0.086(5)	0.080(5)	0.038(5)	0.030(5)	–0.014(4)
C(7)	2*i*	0.1754(7)	0.0777(5)	–0.0253(4)	0.094(5)	0.076(5)	0.076(4)	0.022(4)	0.023(4)	–0.003(4)
C(8)	2*i*	0.2520(7)	0.1631(5)	0.0378(3)	0.091(5)	0.053(4)	0.051(3)	0.028(3)	0.022(3)	0.002(3)
C(9)	2*i*	0.1927(6)	0.2042(5)	0.0859(3)	0.067(4)	0.068(4)	0.057(4)	0.026(3)	0.006(3)	0.002(3)
C(10)	2*i*	0.2738(6)	0.2855(4)	0.1486(3)	0.066(4)	0.058(4)	0.055(3)	0.034(3)	0.015(3)	0.010(3)
C(11)	2*i*	0.2206(6)	0.3221(4)	0.2074(3)	0.054(4)	0.059(4)	0.057(3)	0.028(3)	0.007(3)	0.004(3)
C(12)	2*i*	0.0483(6)	0.3004(6)	0.2634(4)	0.062(4)	0.093(5)	0.095(5)	0.031(4)	0.031(4)	–0.008(4)
C(13)	2*i*	0.1380(7)	0.3740(6)	0.3272(4)	0.073(5)	0.096(5)	0.086(5)	0.038(4)	0.035(4)	–0.003(4)
C(14)	2*i*	0.2740(6)	0.4251(5)	0.3310(3)	0.075(4)	0.081(4)	0.054(4)	0.043(4)	0.018(3)	0.004(3)
C(15)	2*i*	–0.1023(7)	0.2464(7)	0.2556(5)	0.076(5)	0.149(8)	0.140(7)	0.031(5)	0.041(5)	–0.027(6)
C(16)	2*i*	0.3734(6)	0.5070(6)	0.3999(4)	0.086(5)	0.118(6)	0.063(4)	0.036(4)	0.021(4)	–0.018(4)
C(17)	2*i*	0.5950(5)	0.3968(4)	0.3314(3)	0.055(3)	0.056(3)	0.052(3)	0.022(3)	0.020(3)	–0.001(3)
C(18)	2*i*	0.5424(6)	0.3233(5)	0.3824(3)	0.068(4)	0.070(4)	0.060(4)	0.030(3)	0.026(3)	0.011(3)
C(19)	2*i*	0.6242(7)	0.2893(5)	0.4443(4)	0.091(5)	0.065(4)	0.062(4)	0.045(4)	0.025(4)	0.010(3)
C(20)	2*i*	0.5695(8)	0.2117(6)	0.4944(4)	0.135(6)	0.095(5)	0.071(4)	0.064(5)	0.040(5)	0.033(4)
C(21)	2*i*	0.653(1)	0.1813(7)	0.5527(5)	0.156(8)	0.112(7)	0.091(6)	0.067(7)	0.044(6)	0.041(5)
C(22)	2*i*	0.792(1)	0.2242(8)	0.5663(5)	0.142(8)	0.138(8)	0.087(6)	0.083(7)	0.020(6)	0.041(6)
C(23)	2*i*	0.8492(8)	0.2977(7)	0.5203(4)	0.114(6)	0.117(6)	0.073(5)	0.067(5)	0.015(5)	0.018(5)
C(24)	2*i*	0.7668(7)	0.3326(5)	0.4569(3)	0.090(5)	0.073(4)	0.046(3)	0.050(4)	0.013(3)	0.010(3)
C(25)	2*i*	0.8224(6)	0.4071(5)	0.4059(3)	0.065(4)	0.084(4)	0.064(4)	0.039(4)	0.013(3)	0.007(3)
C(26)	2*i*	0.7386(6)	0.4349(4)	0.3439(3)	0.062(4)	0.066(4)	0.051(3)	0.031(3)	0.016(3)	0.005(3)
C(27)	2*i*	0.7890(6)	0.5012(5)	0.2838(3)	0.063(4)	0.065(4)	0.055(3)	0.029(3)	0.018(3)	0.001(3)
C(28)	2*i*	0.7350(7)	0.5723(5)	0.1634(4)	0.083(5)	0.071(4)	0.062(4)	0.032(4)	0.029(4)	0.015(3)
C(29)	2*i*	0.8690(8)	0.6056(5)	0.1641(4)	0.103(6)	0.078(5)	0.090(5)	0.033(4)	0.056(5)	0.026(4)
C(30)	2*i*	0.9600(7)	0.5865(6)	0.2283(5)	0.074(5)	0.087(5)	0.091(5)	0.028(4)	0.039(4)	0.008(4)
C(31)	2*i*	0.6330(7)	0.5915(6)	0.0948(4)	0.130(6)	0.132(7)	0.076(5)	0.073(5)	0.050(5)	0.046(5)
C(32)	2*i*	1.1089(7)	0.6216(7)	0.2327(5)	0.083(5)	0.136(7)	0.136(7)	0.025(5)	0.059(5)	0.017(6)
C(33)	2*i*	0.6714(6)	0.7933(5)	0.3778(4)	0.075(4)	0.063(4)	0.065(4)	0.019(3)	0.021(3)	–0.004(3)
C(34)	2*i*	0.7514(8)	0.7741(6)	0.4477(4)	0.114(6)	0.088(5)	0.084(5)	0.034(5)	–0.013(5)	–0.010(4)
C(35)	2*i*	0.832(1)	0.8556(8)	0.5110(5)	0.159(9)	0.107(7)	0.101(7)	0.036(7)	–0.035(6)	–0.021(6)
C(36)	2*i*	0.832(1)	0.9566(8)	0.5044(6)	0.151(9)	0.107(8)	0.105(7)	0.026(7)	0.002(6)	–0.029(6)
C(37)	2*i*	0.757(1)	0.9782(7)	0.4364(6)	0.156(9)	0.071(5)	0.121(7)	0.024(6)	0.030(7)	–0.017(5)
C(38)	2*i*	0.6763(7)	0.8961(6)	0.3740(4)	0.110(6)	0.069(5)	0.089(5)	0.024(4)	0.006(4)	–0.012(4)
C(39)	2*i*	0.5859(6)	0.7024(5)	0.3115(3)	0.061(4)	0.068(4)	0.056(4)	0.032(3)	0.014(3)	0.004(3)
C(40)	2*i*	0.4988(6)	0.7174(5)	0.2420(4)	0.078(4)	0.059(4)	0.070(4)	0.028(3)	0.012(3)	0.000(3)
C(41)	2*i*	0.4119(6)	0.6427(5)	0.1744(3)	0.063(4)	0.062(4)	0.060(4)	0.033(3)	0.022(3)	0.009(3)
C(42)	2*i*	0.3195(6)	0.6733(5)	0.1072(3)	0.063(4)	0.080(4)	0.055(3)	0.041(3)	0.017(3)	0.013(3)
C(43)	2*i*	0.3106(7)	0.7735(5)	0.1091(4)	0.103(5)	0.091(5)	0.071(4)	0.061(4)	0.028(4)	0.021(4)
C(44)	2*i*	0.2201(8)	0.7952(7)	0.0466(5)	0.139(7)	0.118(7)	0.084(5)	0.096(6)	0.031(5)	0.031(5)
C(45)	2*i*	0.1392(9)	0.7214(8)	–0.0177(5)	0.132(7)	0.162(9)	0.089(6)	0.108(7)	0.005(5)	0.021(6)
C(46)	2*i*	0.1472(9)	0.6222(8)	–0.0215(5)	0.145(7)	0.142(8)	0.101(6)	0.100(7)	–0.042(5)	–0.022(5)
C(47)	2*i*	0.2365(7)	0.5983(6)	0.0417(4)	0.103(6)	0.103(6)	0.093(5)	0.066(5)	–0.016(5)	–0.008(5)
C(48)	2*i*	–0.051(1)	0.899(1)	0.2638(8)	0.21(2)	0.23(2)	0.17(1)	0.06(1)	0.00(1)	0.07(1)
C(49)	2*i*	0.069(2)	0.992(1)	0.248(1)	0.37(3)	0.28(2)	0.24(2)	0.13(2)	0.06(2)	0.16(2)
C(50)	2*i*	0.182(1)	0.959(1)	0.262(1)	0.46(3)	0.36(3)	0.34(2)	0.30(3)	0.22(2)	0.27(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(51)	2*i*	0.298(1)	1.039(1)	0.2357(8)	0.37(2)	0.19(1)	0.19(1)	0.15(2)	0.03(1)	0.11(1)
C(52)	2*i*	0.425(1)	1.0289(9)	0.2799(7)	0.39(2)	0.14(1)	0.19(1)	0.14(1)	0.13(2)	0.06(1)
C(53)	2*i*	0.536(1)	1.0853(9)	0.2422(7)	0.25(1)	0.16(1)	0.20(1)	0.12(1)	0.09(1)	0.090(9)
Ir(1)	2*i*	0.50428(2)	0.46609(2)	0.24659(1)	0.0607(2)	0.0613(2)	0.0486(1)	0.0306(1)	0.0124(1)	0.0049(1)
N(1)	2*i*	0.0878(5)	0.2725(4)	0.2023(3)	0.064(3)	0.083(4)	0.078(3)	0.034(3)	0.018(3)	–0.002(3)
N(2)	2*i*	0.3165(4)	0.4007(4)	0.2679(3)	0.065(3)	0.067(3)	0.051(3)	0.038(3)	0.014(2)	0.004(2)
N(3)	2*i*	0.6930(4)	0.5202(3)	0.2247(3)	0.068(3)	0.052(3)	0.054(3)	0.023(2)	0.020(2)	0.006(2)
N(4)	2*i*	0.9199(5)	0.5338(4)	0.2874(3)	0.061(3)	0.086(4)	0.077(3)	0.028(3)	0.025(3)	0.008(3)
O(1)	2*i*	0.5984(4)	0.6144(3)	0.3262(2)	0.067(2)	0.075(3)	0.056(2)	0.035(2)	0.004(2)	0.002(2)
O(2)	2*i*	0.4037(4)	0.5472(3)	0.1625(2)	0.077(3)	0.064(3)	0.057(2)	0.034(2)	0.006(2)	0.004(2)

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