Lianqing Chen*, Zhongda Wu, Jing Yang and Shijuan Zhang

The synthesis and crystal structure of bis(2-(benzo[d]thiazol-2-yl)-5-methylbenzen-1-ido- κ^2C,N)-(N,N'-diethyldithiocarbamate- κ^2S,S')iridium (III), $C_{33}H_{30}N_3S_4Ir$

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.10 × 0.10 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	4.64 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 Venture, φ and ω
$\theta_{\max}$, completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	19387, 7049, 0.021
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6244
$N(\text{param})_{\text{refined}}$:	375
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Diamond [4]

Source of material

In a representative experiment 2-aminothiophenol, *p*-methylbenzaldehyde, iridium trichloride hydrate, 2-ethoxyethanol and sodium *N,N'*-diethyldithiocarbamate were purchased and used without further purification.

The synthesis of the target compound involves three steps.

In the first step, 2-aminothiophenol (1.250 g, 10 mmol) and *p*-methyl benzaldehyde (1.500 g, 12 mmol) were dissolved to 25 mL of DMSO under argon atmosphere. The mixture was heated at 473.15 K for 2 h. After cooling, the solution was poured into ice water, and then adjusted the solution to pH 8–9 with saturated Na₂CO₃ solution. The precipitate was filtered, washed with a great deal of water several times. After dried under vacuum, the crude product was recrystallized from ethanol, and then obtained white crystalline 2-*p*-tolyl-benzothiazole, yield: 74%. ¹H NMR (CDCl₃, 400 MHz) δ [ppm]: 8.02 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 2.42 (s, 3H). m.p. = 367.15–369.15 K. **Anal.** Calcd. for C₁₄H₁₁NS: C, 74.63; H, 4.92; N, 6.22. Found: C, 74.55; H, 4.97; N, 6.26%. MS (FAB): m/e , 227 (M^+).

In the second step, iridium trichloride hydrate (0.352 g, 1.0 mmol), combined with 2-*p*-tolyl-benzothiazole (0.676 g, 3 mmol), were dissolved in a mixture of 2-ethoxyethanol (30 mL) and water (10 mL), and then refluxed for 12 h. The solution was cooled to room temperature, and the resulting orange red precipitate was collected on by filtration and washed with water and ethanol. After dried under vacuum, the cyclometalated chlorido-bridged dimer was obtained and

<https://doi.org/10.1515/ncrs-2019-0308>

Received April 29, 2019; accepted June 20, 2019; available online July 18, 2019

Abstract

$C_{33}H_{30}N_3S_4Ir$, monoclinic, $P2_1/c$ (no. 14), $a = 11.6429(10)$ Å, $b = 10.9111(10)$ Å, $c = 24.234(2)$ Å, $\beta = 93.2890(10)^\circ$, $V = 3073.6(5)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0198$, $wR_{\text{ref}}(F^2) = 0.0507$, $T = 273(2)$ K.

CCDC no.: 1935444

The molecular structure is shown in the figure (hydrogen atoms are omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Lianqing Chen**, Key Laboratory of Catalysis and Materials Science of the State, Ethnic Affairs Commission and Ministry of Education, South-Central University for Nationalities, Wuhan 430074, P.R. China, e-mail: lqchen@mail.scuec.edu.cn, lqchen_2003@163.com. <https://orcid.org/0000-0003-3706-0683>
Zhongda Wu, Jing Yang and Shijuan Zhang: Key Laboratory of Catalysis and Materials Science of the State, Ethnic Affairs Commission and Ministry of Education, South-Central University for Nationalities, Wuhan 430074, P.R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Ir1	0.31248(2)	0.48167(2)	0.14851(2)	0.03525(4)
S1	0.39058(7)	0.75557(7)	0.28405(3)	0.05916(19)
S2	0.39424(7)	0.28873(8)	−0.00809(3)	0.0609(2)
S4	0.28171(5)	0.26045(5)	0.17137(3)	0.03985(13)
S5	0.11541(5)	0.45445(6)	0.17782(3)	0.04539(15)
N1	0.05807(18)	0.2185(2)	0.18761(11)	0.0533(6)
N2	0.34767(16)	0.56380(19)	0.22420(8)	0.0385(4)
N3	0.29964(18)	0.40841(19)	0.06913(8)	0.0412(5)
C1	0.1406(2)	0.2993(2)	0.18044(10)	0.0402(5)
C2	0.4789(2)	0.4803(2)	0.13019(11)	0.0380(5)
C3	0.5742(2)	0.5318(2)	0.15992(12)	0.0430(6)
H3	0.562036	0.575534	0.192014	0.052*
C4	0.6859(2)	0.5201(2)	0.14325(13)	0.0494(7)
C5	0.7050(3)	0.4549(3)	0.09490(14)	0.0601(8)
H5	0.779632	0.445255	0.083819	0.072*
C7	0.4006(2)	0.3781(2)	0.05068(10)	0.0439(6)
C9	0.2086(3)	0.3627(2)	0.03474(11)	0.0490(6)
C11	0.3658(2)	0.4002(3)	0.29607(11)	0.0491(6)
H11	0.349506	0.336886	0.271157	0.059*
C12	0.3683(2)	0.5206(2)	0.27803(11)	0.0416(6)
C13	0.3930(2)	0.6146(3)	0.31651(12)	0.0505(7)
C14	0.3556(2)	0.6843(2)	0.22194(11)	0.0445(6)
C15	0.5028(2)	0.4198(2)	0.08111(10)	0.0440(6)
C16	0.6150(3)	0.4053(3)	0.06382(12)	0.0552(7)
H16	0.627932	0.362390	0.031594	0.066*
C17	0.2455(3)	0.2931(3)	−0.00920(11)	0.0562(7)
C18	0.3045(2)	0.6599(2)	0.12602(11)	0.0408(5)
C19	0.3316(2)	0.7435(2)	0.16965(12)	0.0447(6)
C20	0.3302(2)	0.8703(3)	0.16122(14)	0.0576(8)
H20	0.348225	0.923517	0.190425	0.069*
C21	0.3018(3)	0.9153(3)	0.10934(15)	0.0633(8)
H21	0.300847	0.999538	0.103453	0.076*
C22	0.2746(3)	0.8363(3)	0.06543(13)	0.0578(7)
C23	0.2761(2)	0.7105(3)	0.07438(12)	0.0497(6)
H23	0.257474	0.658432	0.044834	0.060*
C24	0.4151(3)	0.5890(3)	0.37243(13)	0.0643(8)
H24	0.431829	0.651737	0.397591	0.077*
C25	0.4119(3)	0.4696(3)	0.38958(13)	0.0638(8)
H25	0.425754	0.451187	0.426835	0.077*
C26	0.3880(3)	0.3755(3)	0.35184(12)	0.0577(7)
H26	0.386829	0.294810	0.364196	0.069*
C27	0.0749(3)	0.0869(3)	0.18116(14)	0.0588(8)
H27A	0.039225	0.043869	0.210748	0.071*
H27B	0.156537	0.068651	0.183926	0.071*
C28	−0.0548(3)	0.2575(3)	0.20509(18)	0.0778(11)
H28A	−0.112309	0.197111	0.193453	0.093*
H28B	−0.075867	0.334796	0.187465	0.093*
C29	0.0929(3)	0.3840(3)	0.04026(13)	0.0622(8)
H29	0.067921	0.431816	0.068993	0.075*
C30	0.7863(2)	0.5782(3)	0.17733(14)	0.0666(8)
H30A	0.758342	0.614915	0.209966	0.100*
H30B	0.821609	0.639811	0.155691	0.100*
H30C	0.841915	0.516183	0.187739	0.100*
C31	−0.0528(3)	0.2724(4)	0.26679(19)	0.0967(14)
H31A	−0.124705	0.306354	0.276964	0.145*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H31B	0.008778	0.326431	0.278686	0.145*
H31C	−0.041358	0.193918	0.284144	0.145*
C32	0.0241(4)	0.0427(4)	0.1268(2)	0.1027(16)
H32A	0.057556	0.087009	0.097481	0.154*
H32B	−0.057556	0.055848	0.124958	0.154*
H32C	0.039659	−0.043194	0.122956	0.154*
C33	0.2434(4)	0.8885(3)	0.00814(15)	0.0856(11)
H33A	0.172250	0.932799	0.008798	0.128*
H33B	0.235168	0.822772	−0.018101	0.128*
H33C	0.303228	0.942912	−0.002329	0.128*
C34	0.0154(3)	0.3320(4)	0.00172(14)	0.0789(11)
H34	−0.063022	0.344322	0.004914	0.095*
C35	0.0522(4)	0.2617(4)	−0.04163(15)	0.0833(11)
H35	−0.002005	0.227868	−0.066895	0.100*
C36	0.1662(4)	0.2413(3)	−0.04790(14)	0.0744(10)
H36	0.190540	0.194362	−0.077057	0.089*

the crude product was directly used for next step without further purification.

In the third step, 1.0 mmol of chlorido-bridged dimer, 3.0 mmol of sodium *N,N'*-diethyldithiocarbamate and 10.0 mmol anhydrous sodium carbonate were dissolved in 2-ethoxyethanol. The solution was refluxed under argon for 20 h. After cooling to room temperature, small quantity water was added. The resulting orange precipitate was collected by filtration, washed with water, ethanol and hexane, and dried in vacuum. The crude product was purified by column chromatography on silica gel with CH₂Cl₂/petroleum ether (1:3) as eluent. The target compound were orange powders, yield: 78%. **IR** (KBr, cm^{−1}): 3030, 2987, 1720, 1604, 1503, 852. **¹H NMR** (CDCl₃, 400 MHz): δ (ppm) 8.02 (m, 2H), 7.86 (m, 2H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.39 (m, *J* = 4.4 Hz, 4H), 6.65 (d, *J* = 7.6 Hz, 2H), 6.20 (s, 4H), 5.09 (s, 4H), 1.26 (m, 4H), 0.92 (s, 6H). **Anal.** Calcd. for C₃₃H₃₀N₃S₄Ir: C, 50.23; H, 3.83; N, 5.33. Found: C, 50.26; H, 3.88; N, 5.27%. MS (FAB): *m/e*, 788 (*M*⁺).

Experimental details

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances in the range 0.93–0.98 Å, and with *U*_{iso}(H) = 1.2 *U*_{eq} for aryl H atoms and 1.5 *U*_{eq} for the methyl H atoms. Methyl H atoms were allowed to rotate to best fit the experimental electron density.

Comment

Most recently, heavy metal complexes in OLEDs have attracted much attention as efficient phosphors because they can harvest both singlet and triplet excited states, and thus

the OLEDs internal efficiency can theoretically reach 100% [5]. Especially iridium(III) complexes with cyclometalated ligands show intense phosphorescence at room temperature and this behavior makes them very promising phosphor dyes in OLEDs [6]. Generally, both the luminescent efficiency and emission wavelength of iridium complexes are greatly affected by the heterocyclic ligands [7]. The emission frequency of the iridium complexes can usually be tuned by the introduction of different heterocyclic ligands [8]. Surprisingly, there is very little work to study iridium (III) complexes with thiazole-based heterocyclic ligands [9]. Also, metal complexes containing dithiolato ligands have been extensively studied. However, only relatively few iridium(III) dithiolato complexes have been described.

In the crystal structure of the target compound, the Ir center resides in a distorted octahedral environment. The nitrogen donors of the two chelating 2-(benzo[d]thiazol-2-yl)-5-methylbenzen-1-ido ligands are in *trans* position to each other, the two carbon atoms are in a *cis* configuration, which is in accord with the literature [10]. The Ir—C bonds (2.013(3), 2.021(2) Å) are slightly shorter than the Ir—N bond distances (2.0612(19), 2.081(2)) Å. These values are very similar to those in the analogous complexes reported, such as (ppy)₂Ir(acac) (ppy: 2-(pyridin-2-yl)benzen-1-ido; acac: acetylacetonato)(Ir—C: 2.020(2) Å; Ir—N: 2.090(10) Å) [11]. The similarity of S—C bond lengths (2.5068(7), 2.4585(7)) Å indicate that the charge of the *N,N'*-diethyldithiocarbamate (Et₂dtc) ligand is equally delocalized over both sulfur atoms [12]. The C(2)—Ir(1)—C(18) angle for the complex is 88.71(9)° and the N(2)—Ir(1)—N(3) angle is 171.82(8)°, which are almost equal to the idealized value and well accorded with their *cis*—C—C and *trans*—N—N dispositions, respectively. The Et₂dtc chelate results in an S(5)—Ir(1)—S(4) bond angle of 70.87(2)°, appreciably deviating from the idealized 90° value [13, 14]. The benzothiazole and phenyl moieties in the same cyclometalated ligand are approximately coplanar. The N(2)—Ir(1)—S(5) bond angle of 86.36(5)° indicates that *N,N'*-diethyldithiocarbamate and 2-(benzo[d]thiazol-2-yl)-5-methylbenzen-1-ido are almost perpendicular to each other.

The packing of the target compound exhibit $\pi \cdots \pi$ stacking interactions between aromatic rings in neighboring molecules. There are no classical intermolecular hydrogen bonds and intramolecular hydrogen bonds in the structure. In detail, two molecules form a dimer by the aromatic rings in neighboring molecule and these dimers are connected by $\pi \cdots \pi$ stacking interactions along the *a* axis of the unit cell, with the face-to-face distances of ca. 3.27 Å, constructing a zigzag chain. Zigzag chains are interacted by $\pi \cdots \pi$ stacking interactions along the *b* axis, with the face-to-face distances of ca. 3.32 Å, building up a two-dimensional structure.

The absorption and photoluminescence spectra of the title compound in CH₂Cl₂ solution were investigated. Intense absorptions between 270 and 360 nm can be assigned to the spin allowed π — π^* transitions from cyclometalated ligands. The weaker absorption bands in the range of 325–435 nm can likely be assigned to metal-to-ligand charge transfer (¹MLCT) and π — π^* transition [15]. The complex displays a broad emission at 508 nm, which has good fluorescence quantum yield, and large Stoke's shifts (73 nm). The vibronic fine structures in the PL spectrum imply that the emissions predominantly result from ligand-based π — π^* transition [16].

Acknowledgements: The authors thank the Natural Science Foundation of Hubei province for Distinguished Yong Scholars (No. 2013CFA034); National Natural Science Foundation of China (Grant Nos. 20702064, 21177161 and 31402137); the Program for Excellent Talents in Hubei Province (RCJH15001); the Opening Project of Key Laboratory of Green Catalysis of Sichuan Institutes of High Education (LYZ1107) and the Fundamental Research Funds for the Central University, South-Central University for Nationalities (CZP17077).

References

1. Oxford Diffraction Ltd. CrysAlis^{PRO}, Abingdon, Oxfordshire, England (2006).
2. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Ver. 4.0. Crystal Impact, Bonn, Germany (2015).
5. Wang, Y.; Herron, N.; Grushin, V. V.; Lecloux, D.; Petrov, V.: Highly efficient electroluminescent materials based on fluorinated organometallic iridium compounds. *Appl. Phys. Lett.* **79** (2001) 449–451.
6. Nazeeruddin, M. K.; Humphrybaker, R.; Berner, D.; Rivier, S.; Zuppiroli, L.; Graetzel, M.: Highly phosphorescence iridium complexes and their application in organic light-emitting devices. *J. Am. Chem. Soc.* **125** (2003) 8790–8797.
7. Si, Y.; Zhang, S.; Gahungu, G.; Yang, J.; Wu, Z.: Modification of the emission colour and quantum efficiency for oxazoline- and thiazoline-containing iridium complexes *via* different N-O ligands. *RSC Adv.* **5** (2015) 18464–18470.
8. Tavasli, M.; Moore, T. N.; Zheng, Y.; Bryce, M. R.; Fox, M. A.; Griffiths, G. C.: Colour tuning from green to red by substituent effects in phosphorescent tris-cyclometalated iridium(III) complexes of carbazole-based ligands: synthetic, photophysical, computational and high efficiency oled studies. *J. Mater. Chem.* **22** (2012) 6419–6428.
9. Chen, L.; Yang, C.; Qin, J.; Jia, G.; Han, Y.; Ma, D.: Synthesis, structure, electrochemistry, photophysics and electroluminescence of 1,3,4-oxadiazole-based ortho-metalated iridium(III) complexes. *J. Organomet. Chem.* **691** (2006) 3519–3530.

10. Chen, L. Q.; Qu, X. Y.: Synthesis, characterization and crystal structure of iridium(III)bis(2-*p*-tolyl-benzothiazolato-*N,C*²) (acetylacetonate). *J. Chem. Crystallogr.* **39** (2009) 241–245.
11. Flamigni, L.; Barbieri, A.; Sabatini, C.; Ventura, B.; Barigelletti, F.: Photochemistry and photophysics of coordination compounds: iridium. In: Photochemistry and photophysics of coordination compounds II. Topics in Current Chemistry, vol 281. (Eds. Balzani, V.; Campagna, S.): Springer, Berlin, Heidelberg (2007).
12. Chen, L. Q.: (*N,N*-Diethyldithiocarbamato- $\kappa^2 S, S'$)-bis[2-(2-pyridyl)phenyl- $\kappa^2 C^1, N$]-iridium(III). *Acta Crystallogr.* **E63** (2007) m2078.
13. Chen, L. Q.; Wu, Z. D.: Crystal structure of the phosphorescent complex diethyldithiophosphonato- $\kappa^2 S, S'$ -bis(2-phenylpyridinato- $\kappa^2 C, N$)iridium(III), C₂₆H₂₆N₂O₂PS₂Ir. *Z. Kristallogr. NCS* **234** (2019) 669–671.
14. Katlenok, E. A.; Zolotarev, A. A.; Ivanov, A. Y.; Smirnov, S. N.; Baichurin, R. I.; Balashev, K. P.: Complexes of Ir(III) and Pt(II) with cyclometallated 2-phenylbenzothiazole and chelating diethyldithiocarbamate and *O*-ethyldithiocarbonate ions: structures and optical and electrochemical properties. *Koord. Khim.* **42** (2016) 178–186.
15. Sajoto, T.; Djurovich, P. I.; Tamayo, A.; Yousufuddin, M.; Bau, R.; Thompson, M. E.: Blue and near-UV phosphorescence from iridium complexes with cyclometalated pyrazolyl or *N*-heterocyclic carbene ligands. *Inorg. Chem.* **44** (2005) 7992–8003.
16. Lepeltier, M.; Morlet-Savary, F.; Graff, B.; Lalevée, J.; Gimes, D.; Dumur, F.: Efficient blue green organic light-emitting devices based on a monofluorinated heteroleptic iridium(III) complex. *Synthetic Met.* **199** (2015) 139–146.