ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2017, Vol. 62, No. 8, pp. 1085–1089. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © S.I. Bezzubov, A.A. Bilyalova, I.V. Kuznetsova, K.G. Pavlov, Yu.M. Kiselev, V.D. Dolzhenko, 2017, published in Zhurnal Neorganicheskoi Khimii, 2017, Vol. 62, No. 8, pp. 1087–1091.

Synthesis, Structure, and Optical Properties of Iridium(III) Complex with 1-Benzyl-2-Phenylbenzimidazole and 4,4'-Dicarboxy-2,2'-Bipyridyne

S. I. Bezzubov[a, *], A. A. Bilyalova[b], I. V. Kuznetsova[b], K. G. Pavlov[b], Yu. M. Kiselev[b], and V. D. Dolzhenko[b]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*
[b] *Department of Chemistry, Moscow State University, Moscow, 119991 Russia*
**e-mail: bezzubov@igic.ras.ru*

Received October 12, 2016

Abstract—A new cyclometalated iridium(III) complex [Ir(L)$_2$(Hdcbpy)] (**1**) has been synthesized, where L is 1-benzyl-2-phenylbenzimidazole and Hdcbpy is monoprotonated 4,4'-dicarboxy-2,2'-bipyridine. The structure of complex **1** has been determined by X-ray diffraction. The optical properties of complex **1** have been studied, and the quantum yield of luminescence has been measured.

DOI: 10.1134/S0036023617080046

Recently, cyclometalated complexes (CMCs) of iridium(III) have been considered to be photosensitizers (PSs) for solar cells [1] and hydrogen generation photocatalysts [2]. In both cases, a complex should have noticeable light absorption in the visible region of its spectrum and some other characteristics [3]. The use of 2-arylbenzimidazole derivatives allowed us to obtain a number of iridium(III) complexes possessing the properties required for PSs [4–6]. The regularities of the effect of the nature of both benzimidazole and auxiliary ligands on the electronic structure of iridium complexes and their optical and electrochemical properties were elucidated. In addition, the most promising complexes were successfully tested in solar cells.

On the basis of the data obtained, we assume that, varying substituents in the benzimidazole moiety of the ligands, we will be able to increase the molar absorption coefficients of the corresponding iridium(III) complexes in the visible region of the spectrum. However, this modification of ligands is difficult to obtain because *N*-phenyl derivatives with various substituents in the benzimidazole moiety are difficult to synthesize. Since the nature of the substituent at the nitrogen atom of 2-arylbenzimidazole mainly affects the solubility of the corresponding iridium(III) complex and has no effect on its other properties [6], iridium(III) CMCs with *N*-benzylated 2-arylbenzimidazoles derived from N–H benzimidazoles in one stage [7] are of interest. Here, we present the results of the synthesis and studies of the structure and optical properties of complex [Ir(L)$_2$(Hdcbpy)] (**1**), where L is 1-benzyl-2-phenylbenzimidazole and Hdcbpy is monoprotonated 4,4'-dicarboxy-2,2'-bipyridine.

EXPERIMENTAL

Commercially available pure-for-analysis reagents were used in the work without additional purification. The solvents were distilled and dried according to standard procedures. 1-*H*-2-Phenylbenzimidazole [8] and 4,4'-dicarboxy-2,2'-bipyridine (H$_2$dcbpy) [9] were prepared according to known procedures. The synthesis was carried out in an argon atmosphere; the purification of substances and other manipulations were carried out in air.

1-Benzyl-2-phenylbenzimidazole (L) was prepared by adding benzyl bromide (0.288 g, 1.6 mmol) to a suspension of 1-*H*-2-phenylbenzimidazole (0.294 g, 1.5 mmol) and NaOH (0.120 g, 3 mmol) in DMSO (1 mL) followed by stirring the mixture in an argon atmosphere at 40°C. After 1.5 h, DMSO (0.5 mL) was added, because the mixture became very viscous and did not allow to be mixed. The mixture turned yellow 3 h after the reaction; water (10 mL) was added therein, and the precipitate was filtered off. The precipitate was dissolved in ethanol on heating; the obtained solution was evaporated to dryness, and the resulting precipitate was redissolved in CH$_2$Cl$_2$ (1 mL). Under slow evaporation, colorless needle crystals and yellow oil precipitated, the latter was removed with ether. The remaining crystals were dried in vacuum at 50°C for 2 h. Yield, 180 mg (41%).

Table 1. Crystallographic data and characteristics of data refinement for complex **1**

Parameter	Value
Molecular formula	$C_{52}H_{37}IrN_6O_4 \cdot H_2O$
FW	1890.89
Crystal size, mm	0.25 × 0.20 × 0.08
Syngony	Monoclinic
Space group	$P2_1/c$
a, Å	12.5122(10)
b, Å	13.1980(11)
c, Å	28.035(2)
β, deg	101.415(1)
V, $Å^3$	4538.0(6)
Z	4
P_{calcd}, g/cm^3	1.493
μ, mm^{-1}	2.997
$F(000)$	2040
θ range, deg	2.14–25.05
Index intervals	$-14 \le h \le 14, -15 \le k \le 15,$ $-33 \le l \le 33$
Number of all reflections	31767
Number of unique reflections	8026
Data completeness for θ, %	99.9
Number of parameters	577
F^2	1.001
R_1 for $I > 2\sigma(I)$	0.0375
wR_2 (all data)	0.0765
$\Delta\rho_{max}/\Delta\rho_{min}$, e/$Å^3$	1.360/−1.042

^{1}H NMR ($CDCl_3$), δ, ppm: 5.47 s (2 H), 7.12 d (2 H, J = 6.7 Hz), 7.20–7.26 m (2 H), 7.28–7.37 m (4 H), 7.43–7.51 m (3 H), 7.70 m (2 H), 7.88 d (1 H, J= 8.0 Hz).

Complex [Ir(L)$_2$(Hdcbpy)] (1) was synthesized in two steps. In the first stage, a mixture of 2-ethoxyethanol and water (10 mL, 3/1 vol/vol) was added to $IrCl_3 \cdot 3H_2O$ (27.9 mg, 0.079 mmol) and L (90 mg, 0.306 mmol). The resulting mixture was heated under reflux with stirring under argon for 24 h, cooled, and 3 mL of water was added to the obtained mixture. The precipitate formed was filtered off, washed repeatedly with alcohol and acetone, and dried in vacuum at 50°C for 12 h. The resulting dimeric complex $[Ir(L)_2Cl]_2$ (20 mg) was not characterized and used in the following synthetic stages without additional purification.

In the second stage, the resulting dimer (15.0 mg, 0.009 mmol) and H_2dcbpy (4.4 mg, 0.018 mmol) in a mixture of MeOH and CH_2Cl_2 (1/1 vol/vol, 10 mL) was heated under reflux with stirring under argon in the dark for 16 h. The resulting mixture was cooled, a saturated solution of NH_4PF_6 in methanol (1 mL) was added, and the obtained mixture was stirred for 20 min. The resulting red precipitate was recrystallized from a 1/1 vol/vol mixture of methylene chloride and methanol. The product was dried in vacuum at 50°C for 2 h. A red powder was obtained. Yield, 17.1 mg (21% based on iridium trichloride).

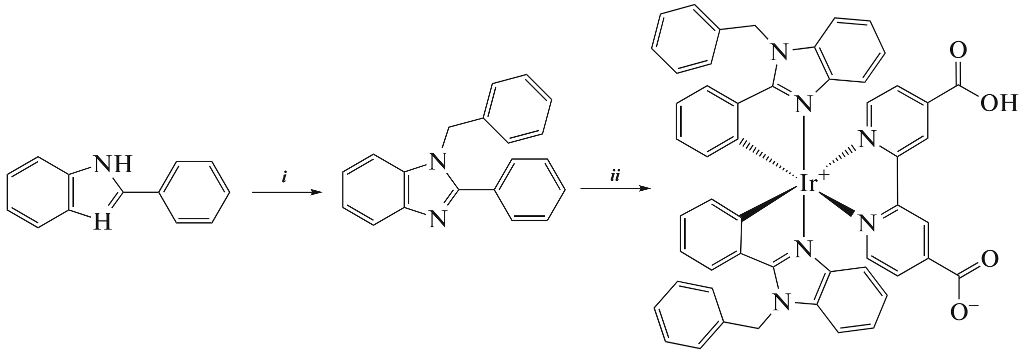
^{1}H NMR (DMSO-d_6), δ, ppm: 5.30 s (4 H), 5.64 d (2 H, J = 8.3 Hz), 5.85–5.99 m (4 H), 6.27 d (2 H, J= 7.0 Hz), 6.74 t (2 H, J = 7.4 Hz), 6.81–7.19 m (9 H), 7.43 d (2 H, J = 8.4 Hz), 7.52–7.61 m (5 H), 7.99 d (2 H, J = 5.7 Hz), 8.22 d (2 H, J = 5.6 Hz), 9.00 s (2 H).

The ^{1}H and ^{31}P NMR spectra were recorded at 25°C on a Bruker Avance 400 spectrometer. The chemical shifts are given in ppm relative to signals from the remained solvent. The electronic absorption spectra were measured on a SF2000 spectrophotometer in quartz cell (1 cm). The luminescence spectra were recorded on a Perkin Elmer LS55 spectrometer. The quantum yield of luminescence was determined relative to Rhodamine 6G.

Single crystals of compound **1** were obtained by slowly evaporating a solution of the complex in a methanol/methylene chloride (1/1 vol/vol) mixture. The experimental data array was collected on a Bruker SMART APEX II diffractometer at 150 K (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) in the ω scan mode. Absorption was taken into account from the measured intensities of equivalent reflections [10]. The structure was solved by a direct method and refined by the full-matrix anisotropic least squares method with respect to F^2 for all non-hydrogen atoms [11]. Hydrogen atoms were placed in the calculated positions and refined according to the "rider" model. A cavity (V= 126 $Å^3$) was found in the crystal of complex **1**. The use of the SQUEEZE procedure [12] showed that this cavity contained five electrons, which is extremely small for a completely occupied solvent molecule. It was not possible to clarify whether a water molecule was present in this cavity. Crystallographic data, details of the experiment and refinement of the structure of **1** are given in Table 1. The full tables of atomic coordinates, bond lengths, and valence angles are deposited with the Cambridge Structural Database: CCDC 1509611 (http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Alkylation of N–H benzimidazoles is usually carried out in the presence of sodium hydride or other bases on heating [7], but we succeeded in simplifying substantially the procedure. 1-Benzyl-2-phenylbenzimidazole (L) was obtained in good yield by the reaction between 1-H-2-phenylbenzimidazole and benzyl bromide in DMSO in the presence of sodium hydroxide as the base (Scheme 1). The isolated ligand was introduced into the cyclometalation reaction with iridium trichloride using the standard procedure [13] to obtain a dimer; the addition of 4,4'-dicarboxy-2,2'-bipyridine (H_2dcbpy) to the obtained dimer afforded a previously unknown Ir(III) complex. Although a saturated methanolic solution of NH_4PF_6 was used to isolate the complex in order to obtain the cationic-anionic compound $[Ir(L)_2(H_2dcbpy)][PF_6]$, zwitterionic complex **1** with a half-dissociated dicarboxylic acid precipitated, with no signals in its ^{31}P NMR spectrum. The composition and structure of the obtained compound were determined by the combined data obtained by the ^1H NMR and X-ray diffraction methods.



L 1

Scheme 1. Synthesis of 1-benzyl-2-phenylbenzimidazole (L) and complex **1**. Reaction conditions: (*i*) benzyl bromide, KOH, DMSO; (*ii*) the first stage is $IrCl_3 \cdot 3H_2O$, 2-ethoxyethanol/water (3/1 vol/vol), the second stage is 4,4'-dicarboxy-2,2'-bipyridine (H_2dcbpy), CH_2Cl_2/CH_3OH (2/1 vol/vol), then an excess of a saturated solution of NH_4PF_6 in CH_3OH.

A molecule of complex **1** is built in a manner typical for these compounds [5, 6]. The central iridium atom is located in a distorted octahedral environment formed by two carbon atoms and two nitrogen atoms of two cyclometalated benzimidazoles and two nitrogen atoms of substituted bipyridine (Fig. 1). The bond

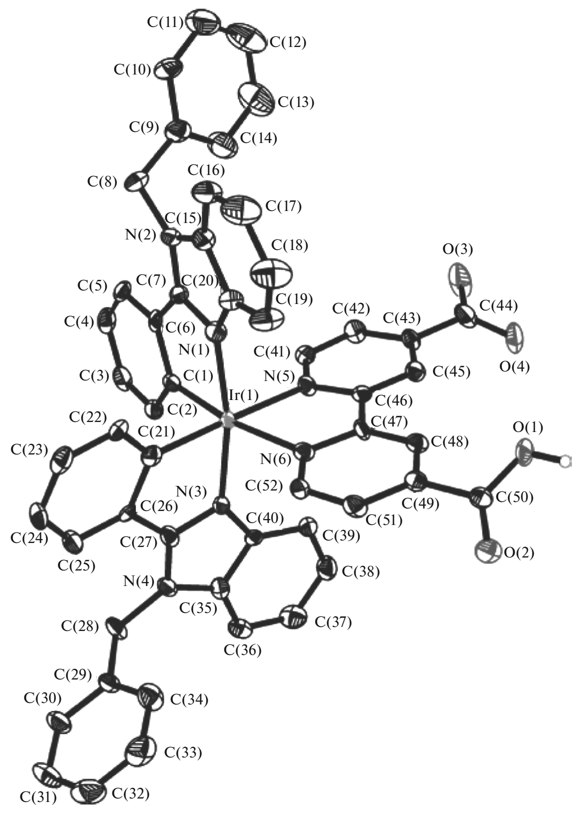


Fig. 1. Molecular structure of complex **1**. Hydrogen atoms are omitted (except for the COOH group). The ellipsoids of atomic thermal vibrations are given with the 50% probability level.

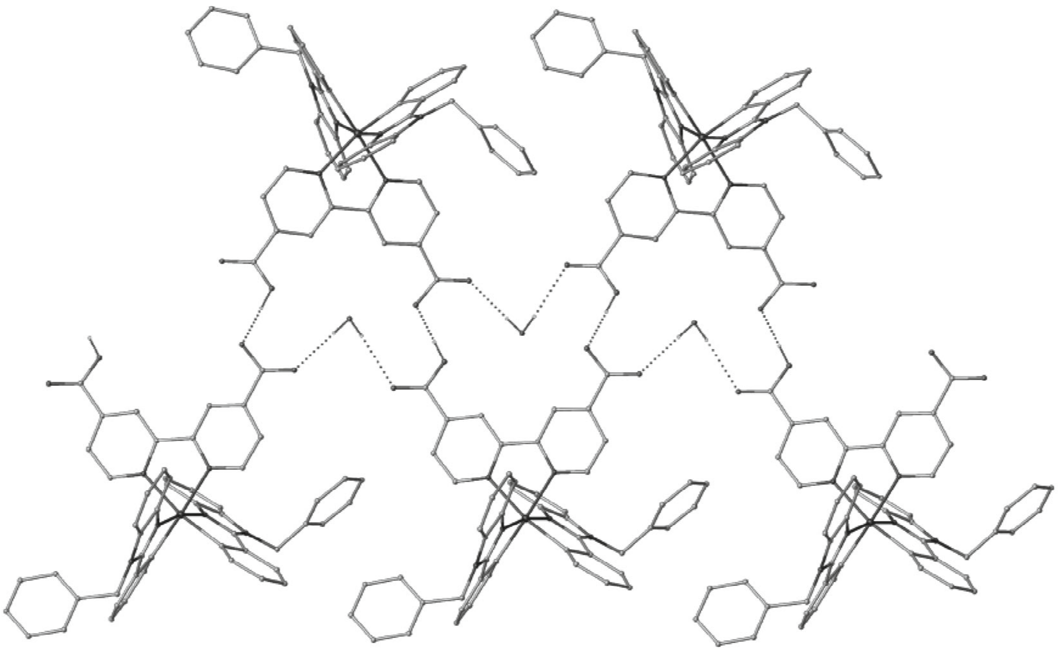


Fig. 2. Crystal packing of complex **1**.

lengths and angles in the coordination environment of the iridium atom are within the limits typical for these complexes (Table 2). The nitrogen atoms of dicarboxybipyridine are more distant from the central atom as compared with the nitrogen atoms of benzimidazoles because of the *trans* effect of Ir—C covalent bonds.

In crystal **1**, the molecules are packed by several hydrogen bonds, some of which are formed by a solvated water molecule acting as a proton donor and forming a bridge (Fig. 2). The presence of a cavity not filled with a solvent in the crystal **1** indicates the high strength of the framework formed by the hydrogen bonds. Apparently, it is a strong package that causes the low solubility of the complex in pure methylene chloride and methanol; however, **1** dissolves in a 1/1 vol/vol mixture of these solvents.

In solution, complex **1** is intensely reddened by noticeable light absorption in the range of 450–600 nm (Fig. 3). This absorption band is due to charge transfer from metal to dcbpy and that from benzimidazole ligands to dcbpy, which we repeatedly observed and interpreted based on the DFT/TDDFT calculations of other Ir(III) complexes [4–6]. Strong absorption bands in the region of 350–400 nm are also caused by a charge transfer of the same nature. Absorption at 300 nm corresponds to $\pi \rightarrow \pi^*$ intraligand electronic transitions. The molar absorption coefficients of complex **1** in the visible region are comparable to those for the above-

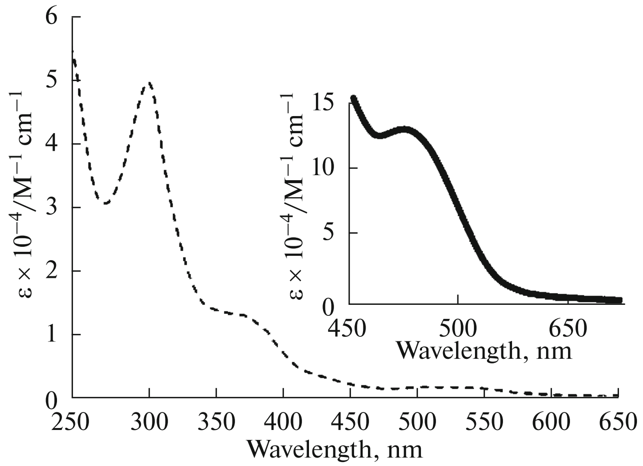


Fig. 3. Electronic absorption spectrum (a 1/1 vol/vol CH_2Cl_2/MeOH mixture, 25°C) of complex **1**.

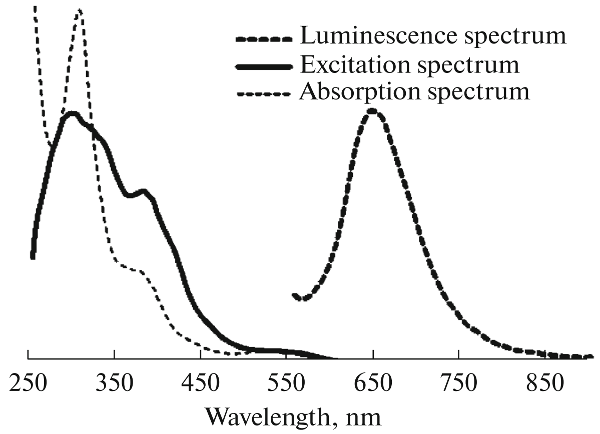


Fig. 4. Luminescence, excitation, and absorption spectra of complex **1** (CH_2Cl_2, 25°C).

Table 2. Selected interatomic bonds (d) and angles (ω) in the structure of **1**

Bond	d, Å	Bond	d, Å
Ir(1)–C(1)	2.009(5)	Ir(1)–N(3)	2.039(4)
Ir(1)–C(21)	2.027(6)	Ir(1)–N(5)	2.135(4)
Ir(1)–N(1)	2.040(5)	Ir(1)–N(6)	2.143(4)
Angle	**ω, deg**	**Angle**	**ω, deg**
C(1)Ir(1)C(21)	89.8(2)	N(3)Ir(1)N(5)	101.16(17)
C(1)Ir(1)N(3)	93.43(19)	N(1)Ir(1)N(5)	87.58(17)
C(21)Ir(1)N(1)	93.1(2)	C(1)Ir(1)N(6)	169.45(19)
N(3)Ir(1)N(1)	168.88(17)	C(21)Ir(1)N(6)	100.64(19)
C(1)Ir(1)N(5)	92.60(19)	N(3)Ir(1)N(6)	90.28(16)
C(21)Ir(1)N(5)	177.60(18)	N(3)Ir(1)N(6)	98.46(17)

Table 3. Optical properties of complex **1**

λ^{abs}, nm ($\varepsilon \times 10^{-3}$, M^{-1} cm^{-1})[a]	λ^{ex}, nm[b]	λ^{lum}, nm[b]	Quantum yield, %[c]
306 (49), 370 (13), 430 (2.7), 510 (1.3)	478	655	5

[a] Measured in a CH_2Cl_2/MeOH mixture (1/1 vol/vol) at 25°C.
[b] Measured in CH_2Cl_2 at 25°C.
[c] Measured in CH_2Cl_2 at 25°C relative to Rhodamine 6G.
Standard error: ±1 nm for λ_{max}, ±1% for ε_{max}, ±5% for quantum yield.

mentioned related complexes based on *N*-phenylbenzimidazoles (1000–3000 M^{-1} cm^{-1}, Table 3).

The study of the luminescence properties of complex **1** in CH_2Cl_2 at room temperature showed that, firstly, the complex emits in the orange region of the spectrum (with a maximum at 655 nm) with a relative luminescence quantum yield of 5% (relative to Rhodamine 6G) and, secondly, the excitation spectrum of **1** almost coincides (in positions of bands) with its absorption spectrum (Fig. 4).

This means that almost all electronic transitions that transfer molecule **1** to the excited singlet state upon light absorption transform it into the radiative triplet state (it has been found that iridium(III) CMCs emit from the triplet level [13]). For comparison, previously we observed the opposite picture exemplified with iridium(III) CMCs with *N*-phenylbenzimidazoles: the absorption spectrum (especially in the visible region) did not coincide with the excitation spectrum. This property of complex **1** that was found here can be considered as an advantage of *N*-benzylbenzimidazoles over other related compounds as ligands for iridium(III) CMCs, since the complex under light absorption should transform as efficiently as possible from the excited singlet state to the triplet state to be applied as a PS. For heavy ions (for example, Ir^{3+}), the triplet state has a significantly longer lifetime, which means that the probability of an electronic transition from the excited PS molecule to a semiconductor is a key step at the operation of Grätzel solar cells [1–3].

Thus, the results of our study we described here show that *N*-benzylbenzimidazoles are a real alternative to *N*-phenylbenzimidazoles in the creation of iridium complexes suitable for the conversion of solar energy into electrical energy, especially since the structure of the former is much easier to modify, including the benzylation method developed in the present work.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, grant no. 16-33-00604mol_a.

REFERENCES

1. A. Sinopoli, C. J. Wood, E. A. Gibson, and P. I. P. Elliott, Eur. J. Inorg. Chem, No. 18, 2887 (2016).
2. J. A. Porras, I. N. Mills, W. J. Transue, and S. Bernhard, J. Am. Chem. Soc. **138**, 9460 (2016).
3. A. Hagfeldt, G. Boschloo, L. Sun, et al., Chem. Rev. **110**, 6595 (2010).
4. S. I. Bezzubov, V. D. Doljenko, S. I. Troyanov, and Yu. M. Kiselev, Inorg. Chim. Acta **415**, 22 (2014).
5. S. I. Bezzubov, V. D. Dolzhenko, and Yu. M. Kiselev, Russ. J. Inorg. Chem. **59**, 571 (2014).
6. S. I. Bezzubov, V. D. Doljenko, Yu. M. Kiselev, et al., Eur. J. Inorg. Chem., No. 3, 347 (2016).
7. S. Hayat, W. Schumann, E. Bayer, et al., Tetrahedron **57**, 9951 (2001).
8. H. F. Ridley, R. G. W. Spickett, and G. M. Timmis, J. Heterocycl. Chem. **2**, 453 (1965).
9. A. M. Oki and R. J. Morgan, Synth. Commun. **25**, 4093 (1995).
10. G. M. Sheldrick, SADABS. Program for Scaling and Correction of Area Detector Data (Univ. of Göttingen, Göttingen, 1997).
11. G. M. Sheldrick, Acta Crystallogr., Sect. A **64**, 112 (2008).
12. A. L. Spek, Acta Crystallogr., Sect. D **65**, 148 (2009).
13. S. Lamansky, P. Djurovich, D. Murphy, et al., J. Am. Chem. Soc. **123**, 4304 (2001).

Translated by V. Avdeeva