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Synthesis of Cyclometalated Platinum(II) Complex with an Alkynyl-Substituted Isocyanide Ligand, Its Structure and Photophysical Properties

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Abstract—The cyclometalated complex of platinum(II) [Pt(ppy)Cl(CNC_6H_4CCPh)] with phenylpyridine and [4-(2-phenylethynyl)phenyl]isocyanide ligands has been synthesized from the [Pt(ppy)Cl]$_2$ dimer and CNC_6H_4C-CPh isocyanide with 90% yield. The compound structure has been characterized using mass spectrometry, IR and NMR spectroscopy methods as well as single-crystal X-ray diffraction. The photophysical properties of the complex in a solid phase have been studied.

Keywords: platinum complexes, isocyanides, luminescence

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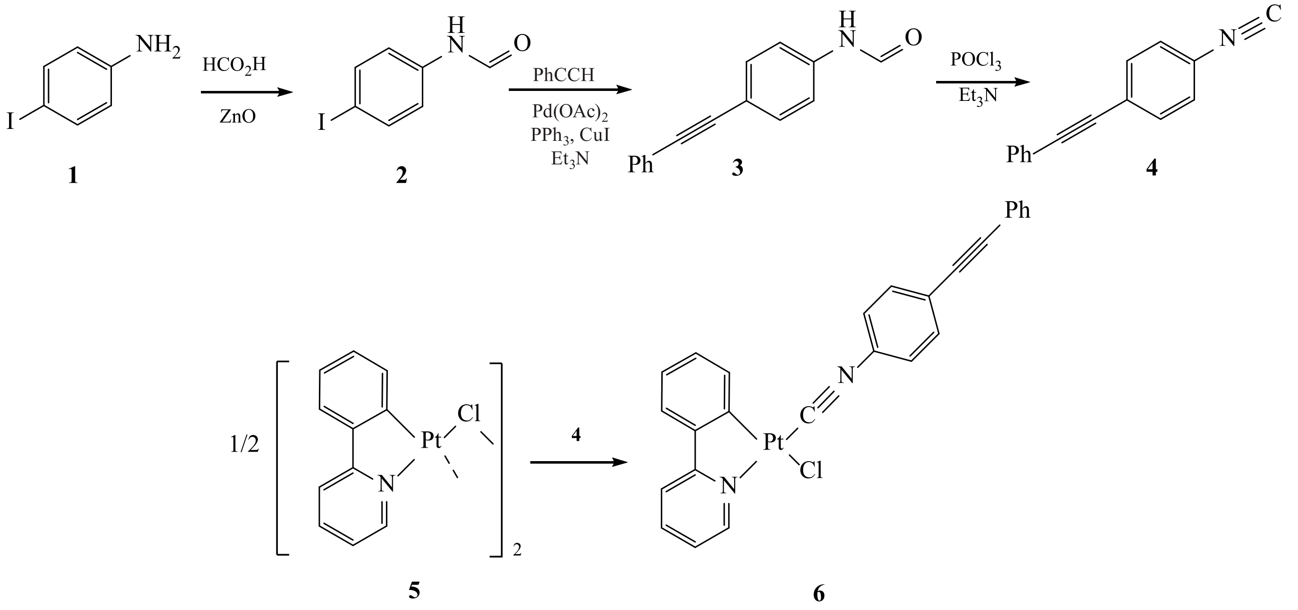
The C,N-cyclometalated platinum(II) complexes are among the most promising organometallic luminophores, displaying the room-temperature luminescence over the entire visible light range [1–3]. They exhibit high efficiency for the photophysical processes of intercombination conversion of the excite singlet state into the lower-energy triplet state, resulting in the efficient phosphorescence [2]. The luminophores based on the heteroleptic C,N-cyclometalated platinum(II) complexes, [Pt(C^N)(L,L')]^z, are the most interesting, since they can emit light over the entire visible range, the wavelength being tuned via the variation of the cyclometalating (C^N) and auxiliary (L, L') ligands [1–3]. The introduction of strong σ-donating ligands (for instance, isocyanides) in the luminophore molecule leads to the increase in the energy difference between HOMO and LUMO levels of the complex and thus to hypsochromic shift of the emission to blue range, affording the luminophores exhibiting high quantum yield [3]. Linear geometry of the isocyanide and the absence of steric hindrance facilitate the formation of the metallophilic Pt···Pt interactions and the π–π-stacking which enhance the structural rigidity of the molecules, thus reducing the radiationless energy scattering [4, 5]. Certain cyclometalated platinum(II) complexes with isocyanide ligands exhibiting promising photophysical [1, 6–8] and photocatalytic [9–11] properties have been described, yet the range of the isocyanide ligands used in these studies has been limited. It should be underscored that the C,N-cyclometalated platinum(II) complexes containing one halide and one isocyanide group as the auxiliary ligands have been extremely scarce [5, 12–15]; such complexes for cyclometalated 2-phenylpyridine have not been mentioned.

Moreover, the isocyanide ligands can be involved in the nonvalent interactions [9–22] which allow the tuning of photophysical parameters of the luminescent materials. The low energy of such interactions makes the involved processes reversible, fast, and readily tunable [23–26]. In this regard, the presence of a lengthy system of the conjugated bonds and the absence of bulky substituents are the key factors in the choice of the isocyanide ligand. Herein we investigated the preparation of such complexes exemplified by compound **6** containing 4-(phenylethynyl)-phenyl substituent (Scheme 1).

Isocyanide **4** was synthesized via synthetic Scheme 1. Formamide **3** was prepared from 4-iodoaniline **1** in two stages involving the formation of formamide **2** and its Sonogashira cross-coupling with phenylacetylene. The addition of equimolar amount of compound **4** to a suspension of the chloride-bridged dimer **5** in 1,2-dichloroethane followed by 2 h refluxing afforded

Scheme 1.



the [Pt(ppy)Cl(CNC_6H_4CCPh)] complex **6** in good yield (90%).

Complex **6** was isolated as light yellow crystalline solid (decomposing at 171°C) and characterized by means of mass spectrometry as well as IR and NMR spectroscopy. Its solid-state structure was elucidated by single-crystal X-ray diffraction (Fig. 1).

Mass spectrum of complex **6** contained the strongest peak assigned to the $[M-\mathrm{Cl}]^+$ ion with the characteristic isotopic distribution. The IR spectrum of the complex contained a strong band of the C≡N bond stretching at 2176 cm^{-1}, being in good agreement with the reference data on isocyanide complexes of platinum [27–29]. Moreover, the following bands were observed: C–H stretching (3054 cm^{-1}), C–C ring deformation (1604, 1502 cm^{-1}), C–H in-plane deformation (1066 cm^{-1}), and C–H out-of-plane deformation (841, 756, 689 cm^{-1}).

^{1}H NMR spectrum of complex **6** contained a set of signals in the spectral range typical of the aromatic protons, assignable to those of the ppy and isocyanide fragments. A distinctive high-frequency signal at 9.58 ppm was assigned to the H^{11} proton (see the enumeration in Fig. 1) of the ppy group, the downfield shift being due to its strong deshielding by the nitrogen atom [30, 31]. The signal multiplicity was owing to the splitting at the ^{195}Pt nucleus [30, 31]. The ^{13}C NMR spectrum revealed that the signals of the carbon atoms nearest to the platinum atom (C^1, C^7, C^{11}) were also split at the ^{195}Pt nucleus. The signal of the carbon atom of the isocyanide group at 131.1 ppm was weak, which was typical of such complexes [27, 32, 33]. Furthermore, the ^{13}C NMR signals at 87.8 and 93.0 ppm were assigned to the carbon atoms at the triple C≡C bond. The platinum atom signal in the ^{195}Pt NMR spectrum of complex **6** was found at –3880 ppm, being typical of the isocyanide platinum(II) complexes [27, 32, 33].

The solid-state structure of complex **6** was elucidated by means of single-crystal X-ray diffraction (Fig. 1). The values of the selected bond lengths and angles are collected in Table 1.

The crystallographically independent part of structure **6** was represented by a single [Pt(ppy)Cl(CNC_6H_4CCPh)] molecule (Fig. 1). The carbon atoms of the phenylpyridine and isocyanide moieties coordinated to platinum(II) were in the *cis* configuration. The platinum–carbon bond of the isocyanide fragment was 0.1 Å shorter than that with the carbon atom of the cyclometalated ligand. Other bond lengths were in good agreement with the known

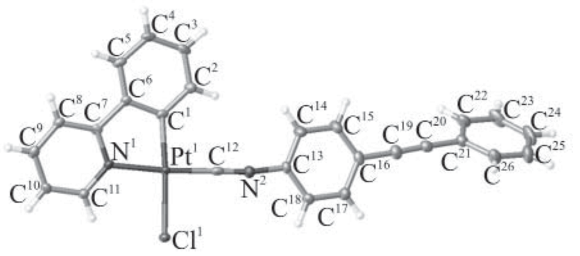


Fig. 1. General view of a molecule of complex **6** in the crystal (CCDC 1956173).

Table 1. Selected bond lengths and angles in complex **6**

Bond length	*d*, Å	Angle	φ,deg
$Pt^1–Cl^1$	2.388(1)	$C^1Pt^1N^1$	80.97(15)
$Pt^1–N^1$	2.055(3)	$C^{12}Pt^1Cl^1$	89.85(34)
$Pt^1–C^1$	1.997(4)	$C^{12}N^2C^{13}$	169.5(4)
$Pt^1–C^{12}$	1.888(4)	$N^2C^{12}Pt^1$	179.1(4)
$N^2–C^{12}$	1.150(5)	$C^{19}C^{20}C^{21}$	176.6(5)
$C^{20}–C^{19}$	1.203(6)	$C^{20}C^{19}C^{16}$	176.9(5)

interatomic distances in isocyanide platinum(II) and palladium(II) complexes [27, 32, 33].

The metallophilic Pt···Pt interactions typical of bis-isocyanide platinum(II) complexes [35] were not observed in the structure of complex **6**. To elucidate the interatomic contacts contributing to the crystal packing, we performed the Hirshfeld surface analysis for structure **6** [36]. The following fractional contributions of the interatomic contacts were revealed (%): C–H 37.4, H–H 35.9, Cl–H 9.0, C–C 7.1, N–H 3.4, Pt–H 2.3, C–N 1.8, C–Cl 1.4, Pt–C 1.0, and N–Cl 0.7. Hence, the Hirshfeld surface analysis of structure **6** showed that the interatomic interactions involving hydrogen atoms determined the crystal packing of the compound. However, the presence of the C–C and C–N contacts between the atoms involved in the π–π-interactions as well as the contacts with the platinum atoms which could affect the photophysical properties of the complex should be underestimated.

The photophysical properties of the prepared complex **6** in a solid state were investigated (Fig. 2): the absorption and emission spectra were recorded, and the excited state lifetime was measured.

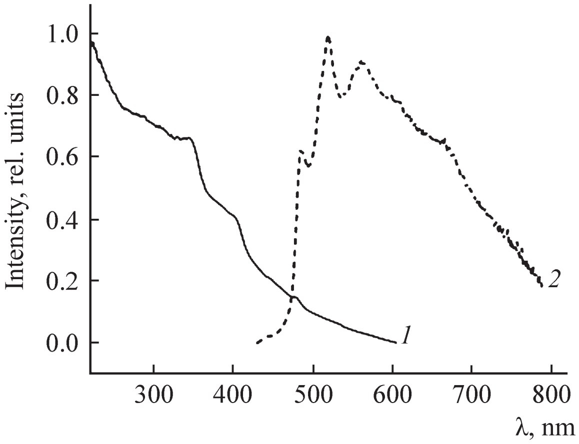


Fig. 2. Absorption (*1*) and emission (*2*) spectra of complex **6** in solid state (293 K).

The absorption spectrum of complex **6** (Fig. 2) contained a strong band at λ = 350 nm which could be assigned to the intraligand π–π*-transitions. The weaker bands at λ = 410 nm were likely due to the intraligand charge transfer (^{1}ILCT) [ppy, π→π*], the ligand to ligand charge transfer [^{1}LL$_0$CT (L = ppy, L$_0$ = CNC_6H_4CCPh)], and the metal to ligand charge transfer (^{1}MLCT) [*d*σ*(Pt)→(π*, ppy)] as well as the mixed-ligand charge transfer ^{1}MLCT/^{1}ML$_0$CT. The observed bands practically coincided with the positions of the corresponding bands for other similar monoisocyanide complexes [M(C^N) Cl(CNR)] [5–7, 12].

In the red part of the spectrum contained a low absorption band at λ = 480 nm which could be assigned to the spin-allowed charge transfer from the metal–metal–ligand bond (^{1}MMLCT) due to the [*d*σ*$(Pt)_2$→(π*, ppy)] and [σ*(π, ppy)→σ(π*, ppy) transfer [7, 8, 37]. Therefore, the presence of that band pointed at the interaction with the platinum atom and the π–π-interactions.

The emission spectrum of complex 6 revealed vibrationally structured with maximum of emission, which was in agreement with the corresponding data for the [M(C^N)Cl(CNR)] monoisocyanide complexes [7, 15, 38]. The bands at λ = 485, 519, and 560 nm were due to the transfers assigned to the cyclometalated ppy ligand (^{3}IL and ^{3}ILCT) as well as to the mixed-ligand contribution owing to the ^{3}MLCT/^{3}ML$_0$CT tranfer (L = ppy, L$_0$ = CNC_6H_4CCPh). The contribution from the ^{3}MMLCT transfers led to the appearance of an additional band at λ = 650 nm and the shift of the bands to the long-wave part.

The lifetime of the excited state of complex **6** was of the microsecond range (0.8 μs), evidencing the triplet nature of the excited state [5, 37].

In summary, the possibility of the preparation of cyclometalated platinum(II) complexes containing arylisocyanide with the extended conjugation chain as one of the auxiliary ligands was demonstrated using the [$Pt(ppy)Cl(CNC_6H_4CCPh)$] complex as the example.

EXPERIMENTAL

The starting chemicals and solvents were purchased from Aldrich and used as received, except for 1,2-dichloroethane, CH_2Cl_2, THF, and Et_2O. 1,2-Dichloroethane and CH_2Cl_2 were distilled over P_2O_5, THF was distilled over CaO, and Et_2O was distilled over sodium metal in the presence of benzophenone. The chlorine-bridged complex **5** was prepared from $K_2[PtCl_4]$ as described elsewhere [30].

Mass spectrometry analysis was performed using a Bruker micrOTOF instrument (Bruker Daltonics) in the electrospray ionization mode with methanol as solvent. The *m/z* values were reported for the strongest signals of the isotopologs. IR spectra were recorded using a Shimadzu FTIR 8400S spectrometer (4000–400 cm^{-1}, KBr pellets). ^1H, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra of the solutions in $CDCl_3$ were recorded using a Bruker Avance II+ spectrometer [400.13 (^1H), 100.61 (^{13}C), and 86 MHz (^{195}Pt)] at room temperature. Absorption spectra were recorded using a UV-1800 spectrophotometer. Excitation and emission spectra as well as the luminescence lifetime were studied using a Fluorolog-3 spectrofluorimeter (Horiba Jobin Yvon).

***N*-(4-Iodophenyl)formamide (2)** [39]. ZnO (2.754 g, 0.034 mol) was added portionwise to 45 mL of 85% formic acid (54.9 g, 1.2 mol) at cooling. The obtained suspension was stirred during 15 min, and then 4-iodoaniline (15 g, 68 mmol) was added. The mixture was heated at 75°C during 2 h until the conversion of the starting aniline was complete (TLC monitoring). The mixture was cooled to room temperature, diluted with 100 mL of CH_2Cl_2, and filtered to remove ZnO. The filtrate was washed with saturated solution of sodium hydrocarbonate to neutral reaction of the medium. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum; the residue was purified via chromatography on silica gel [eluent: hexane–ethyl acetate (1 : 1)]. Yield 13.4 g (80%). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.85 d (1H, ArH, $^3J_{HH}$ = 8.6 Hz), 7.33 m (1H, ArH), 7.63–7.68 m (2H, ArH), 8.39 s (1H, NH), 8.65–8.70 m (1H, HCO).

***N*-{4-[(2-Phenyl)ethynyl]phenyl}formamide (3)** [40]. A mixture of 47 mg (0.21 mmol) of $Pd(OAc)_2$, 118 mg (0.45 mmol) of PPh_3, 44 mg (0.73 mmol) of CuI, and 10 mL of THF was stirred during 30 min under argon atmosphere, and then 1.15 g (4.7 mmol) of *N*-(4-iodophenyl)formamide **2**, 0.51 g (5 mmol) of phenylacetylene, and 0.10 g (10 mmol) of triethylamine were added in sequence. The reaction mixture was stirred at 60°C during 4–6 h. After the reaction was complete, the mixture was cooled to room temperature, filtered through celite, and washed with CH_2Cl_2 (3×50 mL). The solvent was evaporated off; the product was isolated via recrystallization from methanol and dried under vacuum. Yield 0.61 g (59%). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.06 d (1H, ArH, $^3J_{HH}$ = 8.5 Hz), 7.33–7.38 m (3H, ArH), 7.50–7.56 m (5H, ArH), 8.40 s (1H, NH), 8.75 d (1H, HCO, $^3J_{HH}$ = 11.3 Hz), 8.39 br. s (1H, NH), 8.65–8.67 m (1H, HCO).

1-Isocyano-4-[(2-phenyl)ethynyl]benzene (4) [40]. A mixture of 0.3 g (1.36 mmol) of formamide **3** in 10 mL of distilled CH_2Cl_2 was cooled to –10°C and stirred during 15 min under argon; 0.62 mL (0.4 g, 11.9 mmol) of triethylamine and then 0.14 mL (230 mg, 1.5 mmol) of $POCl_3$ (dropwise over 1 h) were added. The obtained mixture was stirred during 2 h at –10 to 0°C; after that, a solution of sodium hydrocarbonate was added, and the mixture was stirred during 10 min at room temperature. The organic layer was separated, washed with CH_2Cl_2 (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was evaporated under vacuum, and the residue was purified via chromatography on silica gel [eluent: hexane–ethyl acetate (5 : 1)]. Yield 194 mg (70%). IR spectrum, ν, cm^{-1}: 2125 (N≡C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.35–7.38 m (4H, ArH), 7.52–7.55 m (5H, ArH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 126.46 (C≡N), 92.20, 87.31 (C≡C); 132.56, 131.70, 128.88, 128.47, 124.82, 122.49 (C_{Ar}).

[Pt(ppy)Cl(CNC_6H_4CCPh)] (6). A solution of isocyanide **4** (53 mg, 0.26 mmol) in 10 mL of 1,2-dichloroethane was added dropwise over 1 h to a suspension of $[Pt(ppy)Cl]_2$ (100 mg, 0.13 mmol) in 20 mL of 1,2-dichloroethane at stirring and heating to 50°C. The obtained mixture was stirred at 80°C during 2 h and evaporated to minimal volume; 10 mL of Et_2O was then added. The precipitate was separated off and recrystallized from a CH_2Cl_2–Et_2O mixture (2 : 1). Yield 138 mg (90%), decomp. 171°C. IR spectrum, ν, cm^{-1}: 2176 (N≡C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.13 t. d (1H, H^3, ppy, $^3J_{HH}$ = 6.7, 1.3 Hz), 7.19 t. d (1H, H^4, ppy, $^3J_{HH}$ = 7.4, 0.9 Hz), 7.31 t (1H, H^{10}, ppy, $^3J_{HH}$ = 6.1 Hz), 7.37–7.39 m (3H, $C{\equiv}CC_6H_4$), 7.59–7.52 m (5.5H, $C_6H_4C{\equiv}CC_6H_4$ + H^2 + H^5, ppy), 7.61–7.3 m (2H, $C{\equiv}NC_6H_4$), 7.73–7.77 m (1H, H^8, ppy), 7.90 t. d (1H, H^9, ppy, $^3J_{HH}$ = 7.8, 1.3 Hz), 9.58 d (1H, H^{11}, ppy, $^3J_{HH}$ = 5.0, $^3J_{PtH}$ = 28.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 87.78, 92.96 (C≡C), 118.57 (C^8, ppy), 122.26 (C^{10}, ppy), 122.42 ($C_6H_4C{\equiv}CC_6H_4$), 124.24 (C^5), 124.77 (C^4), 125.56, 126.56, 128.50, 128.99 ($C_6H_4C{\equiv}CC_6H_4$), 131.14 (C≡N), 131.50 (C^3, ppy), 131.75 and 132.83 ($C_6H_4C{\equiv}CC_6H_4$), 136.16 (C^2, ppy), 140.31 (C^9, ppy), 141.39 (C^1, ppy), 144.02 (C^6, ppy), 148.99 (C^{11}, ppy), 166.39 (C^7, ppy). $^{195}Pt\{^1H\}$ NMR spectrum ($CDCl_3$):

δ_{Pt} –3880 ppm. Mass spectrum, *m/z*: 552.0992 $[M - Cl]^+$ (calculated for $C_{26}H_{17}N_2Pt^+$: 552.1036).

X-ray diffraction analysis of complex **6** was performed using an Xcalibur, Eos diffractometer. The measurement was performed at 100 K using monochromatic MoK_α radiation ($\lambda = 0.71073$ nm). The unit cell parameters were refined via least squares method basing on 35525 reflections with 2θ 5.186–54.996°. The structure was solved via direct methods and refined to $R_1 = 0.0271$ ($wR_2 = 0.0669$) over 4652 independent reflections with $|Fo| \geq 4\sigma F$ using SHELX software [41, 42] available in OLEX2 package [43]. Empirical correction for absorption was performed using CrysAlisPro software package via spherical harmonics implemented in the SCALE3 ABSPACK scaling algorithm [44].

Complex 6. $C_{26}H_{17}ClN_2Pt$, $M = 587.95$, monoclinic crystal system, space group $P2_1/c$, $a = 18.3454(4)$ Å, $b = 5.34210(10)$ Å, $c = 22.22.1852(4)$ Å, $\beta = 110.499(2)°$, $V = 2036.54[38]$ Å^3, $Z = 4$, $d_{calc} = 1.918$ g/cm^3, $\mu = 7.037$ mm^{-1}, 4652 independent reflections with $I > 2\sigma(I)$, $R_1(|F_o| \geq 4\sigma_F)/R_1$ (over all data) = 0.0271/0.0313, wR_2 $(|F_o| \geq 4\sigma_F)/wR_2$ (over all data) = 0.0669/0.0699, $S = 1.054$, $\rho_{min}/\rho_{max} = 1.39/–1.63$ e/Å^3.

The Hirshfeld surface analysis of the complex **6** crystal structure was performed in the frame of normalized contact lengths (dnorm) [42] based on Bondi van der Waals radii [45], as implemented in CrystalExplorer 3.1 software.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

SUPPLEMENTARY MATERIALS

Supplementary materials are available for this article at https://doi.org/10.1134/S1070363220040143 and are accessible for authorized users.

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