Short Note

(2-[4-Methylpyrazol-1-yl]phenyl)platinum(II)
(1,3-bis[1-methyl-1H-pyrazol-4-yl]propane-1,3-dione)

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Abstract: In this work, the title compound was synthesized via the reaction of an aryl-substituted pyrazole with potassium tetrachloroplatinate, followed by the reaction of the postulated intermediate chloro-bridged dimer with a pyrazole-containing 1,3-diketonate ligand. The structure of the synthesized complex was established by $^1$H, $^{13}$C NMR spectroscopy and mass spectrometry. According to UV-Vis spectrometry studies, the obtained complex exhibits green fluorescence with a maximum at 514 nm. Based on cyclic voltammetry studies, the HOMO, LUMO and band gap values were calculated.

Keywords: platinum(II) complex; metallocycles; organic light-emitting diode; pyrazole

1. Introduction

Platinum-group metal complexes are the most important family of phosphor material for modern photovoltaic devices [1]. While iridium(III) complexes are the most studied and widely used class [2], platinum(II) complexes are less common [3]. The combination of a Pt(II) core with organic ligands can lead to the formation of a wide variety of complexes with intriguing properties, especially cyclometalated Pt(II) complexes, which are efficient organic light-emitting structures [4].

The photophysical and photochemical properties of Pt(II) complexes are strongly dependent on the type of the coordinating ligands [5]. Pt(II) complexes bearing monodentate ligands are known to exhibit poor luminescence. On the other hand, the transition to bidentate ligands qualitatively changes the electronic configuration of the complexes, significantly promoting their photophysical properties [6]. Among them, of greatest interest are Pt(II) complexes, consisting of two types of bidentate ligands—C=N, represented predominantly by aryl-substituted N-heterocyclic compounds, and O=O ligands, such as 1,3-dicarbonyl compounds [7].

The variety of suitable C=N ligands for successful and stable complexation is constantly expanding, providing the ability to fine-tune the electronic and photophysical parameters of Pt(II) complexes. However, the range of 1,3-dicarbonyl ligands is mainly limited to dialkylolymethane (acetylacetone, dipivaloylmethane) and diaroylmethane (dibenzyloxymethane). To date, there are little to no examples of Pt(II) complexes with a heterocyclic 1,3-dicarbonyl ligands presented in the literature. In this work, a two-step synthetic protocol leading to the formation of heteroleptic Pt(II) complex 4 containing a pyrazole-based 1,3-dicarbonyl ligand was developed (Scheme 1).
Scheme 1. Synthesis of (2-[4-methylpyrazol-1-yl]phenyl)platinum(II) (1,3-bis[1-methyl-1H-pyrazol-4-yl]propane-1,3-dione) (Pt(mpp)(bmppd)) 4.

2. Results and Discussion

At the first stage, the contact between 4-methyl-1-phenyl-1H-pyrazole (1) and potassium tetrachloroplatinate(II) was initiated. The reaction proceeds under reflux conditions for 12 h under an argon atmosphere in 2-ethoxyethanol–water mixture. In this process, 1 acts as cyclometallating C^N ligand, while K₂PtCl₄ is employed as a platinum source.

The resulting postulated chloro-bridged dimer complex (2) was used in the next step without purification. The reaction with pyrazole-based 1,3-dicarbonyl ligand 3 was carried out for 15 h at 100 °C in 2-ethoxyethanol. Sodium carbonate was used as the base. The resulting yellow complex 4 precipitates from the reaction mixture after the addition of water. After chromatographic purification, the structure of complex 4 was confirmed by ¹H and ¹³C NMR spectroscopy, FT-IR spectroscopy and high-resolution mass spectrometry (Figures S1–S4, Supplementary Materials). The absorption and emission spectra of Pt(mpp)(bmppd) are presented in Figure 1a. The CHCl₃ solution of complex 4 exhibits green light emission at a maximum of 514 nm upon photoexcitation at 325 nm. The cyclic voltammetry curves of 4 are shown in Figure 1b. Based on CV studies, the calculated values of the HOMO and LUMO of complex 4 are -4.98 eV and -2.54 eV, respectively, leading to a band gap value of 2.44 eV (Equations (1)–(3)) that correlates to the observed photoluminescence in the green region.

![Figure 1](image)

**Figure 1.** (a) The normalized absorption and emission spectra of Pt(mpp)(bmppd) in 5 × 10⁻⁶ mol/L CHCl₃ solution (λ_ext. = 325 nm). (b) Cyclic voltammogram of Pt(mpp)(bmppd) in 4 × 10⁻³ mol/L DMF (solid line) and background (dashed line) (0.1 M Bu₄NBF₄).

Values of HOMO, LUMO and band gap for complex 4 were calculated as follows:

\[
E_{\text{HOMO}} = -\left( E_{\text{onset}}^{\text{fl}} - E_{\text{onset}}^{\text{fl}}(\text{Fc}) + 4.78 \right) = -(0.68 - 0.48 + 4.78) = -4.98 \text{ eV} \quad (1)
\]

\[
E_{\text{LUMO}} = -\left( E_{\text{onset}}^{\text{fl}} - E_{\text{onset}}^{\text{fl}}(\text{Fc}) + 4.78 \right) = -(1.94 - 0.30 + 4.78) = -2.54 \text{ eV} \quad (2)
\]

\[
\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} = -2.54 - (-4.98) = 2.44 \text{ eV} \quad (3)
\]
3. Materials and Methods

3.1. General

4-Methyl-1-phenyl-1H-pyrazole (1) [8] and 1,3-bis(1-methyl-1H-pyrazol-4-yl)propane-1,3-dione (3) [9] were prepared according to the published methods. All commercially available reagents and solvents were used without purification. Chromatography of the final product was performed on silica gel (0.060–0.200 mm, 60 Å, CAS 7631-86-9). $^1$H and $^{13}$C NMR spectra were taken with a Bruker AM-300 instrument (at frequencies of 300 and 75 MHz, Billerica, MA, USA) in CDCl$_3$ using the residual solvent peak as a reference. J values are given in Hz. The high-resolution mass spectrum was measured on a Bruker microTOF II instrument (Billerica, MA, USA) using electrospray ionization (ESI). FT-IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer (Billerica, MA, USA). Solution UV–visible absorption spectra were recorded using an Agilent Cary 60 UV–Vis spectrophotometer (Santa Clara, CA, USA) in standard 10 mm photometric quartz cells in HPLC-grade CHCl$_3$ at a concentration of 10$^{-4}$ M. Luminescence spectra were recorded using an Agilent Cary Eclipse (Santa Clara, CA, USA) in HPLC-grade CHCl$_3$. Cyclic voltammetry was implemented on an Econix IPC-Pro M potentiostat (Moscow, Russia) at a scan rate of 100 mV·s$^{-1}$ using three electrode cells, equipped with a glassy-carbon working electrode, platinum auxiliary electrode and Ag/Ag$^+$ reference electrode. Electrochemical experiments were performed under an argon atmosphere to prevent reduction and other side reactions with atmospheric oxygen.

3.2. (2-[4-Methylpyrazol-1-yl]phenyl)platinum(II) (1,3-bis[1-methyl-1H-pyrazol-4-yl]propane-1,3-dione) (Pt(mpp)(bmppd)) (4)

A Schlenk tube under Ar atmosphere was charged with 158 mg (1.0 mmol) of 4-methyl-1-phenyl-1H-pyrazole (1) and 208 mg (0.5 mmol) of K$_2$PtCl$_4$ in 5 mL of water–2-ethoxyethanol mixture (1:3 v/v). Reaction mixture was heated while stirring for 12 h at 100 $^\circ$C. After the cooling, 15 mL of water was added and the precipitate of the dimer complex (2) was separated, washed with water and dried at 80 $^\circ$C to a constant weight. To the resulting solid, 5 mL of 2-ethoxyethanol was added, followed by the addition of 348 mg (1.50 mmol) of 1,3-bis(1-methyl-1H-pyrazol-4-yl)propane-1,3-dione (3) and 1 g (9.50 mmol) of Na$_2$CO$_3$. The resulting suspension was stirred at 100 $^\circ$C for 15 h and then cooled and quenched by the addition of water (15 mL). The yellow solid was separated, washed with water, dried at 100 $^\circ$C at 0.1 Torr and purified by column chromatography (silica gel/dichloromethane-methanol 20:1 v/v). Yield—192 mg (33%) of yellow solid, Rf = 0.71 (dichloromethane-methanol 20:1 v/v). $^1$H NMR (CDCl$_3$, ppm): δ 8.00–7.87 (m, 4H), 7.75 (s, 1H), 7.64 (s, 1H), 7.61–7.53 (m, 1H), 7.15–7.03 (m, 3H), 6.20 (s, 1H), 3.97 (s, 6H), 2.21 (s, 3H). $^{13}$C NMR (CDCl$_3$, ppm): δ 139.1, 138.6, 137.5, 131.5, 131.0, 130.9, 124.7, 124.6, 124.5, 124.0, 122.3, 109.9, 96.5, 39.5, 9.7. HRMS (ESI-TOF), m/z: calcd for C$_{21}$H$_{20}$N$_5$O$_2$Pt [M + H]$^+$, 584.1370, found, 584.1361.

4. Conclusions

The previously unknown cyclometallated platinum (II) complex (2-[4-methylpyrazol-1-yl]phenyl)platinum(II) (1,3-bis[1-methyl-1H-pyrazol-4-yl]propane-1,3-dione) (Pt(mpp)(bmppd)) (4) was synthesized with a yield of 33%. The structure of the compound was confirmed by NMR spectroscopy and high-resolution mass spectrometry. The obtained complex was characterized with UV/Vis spectroscopy and cyclic voltammetry.

Supplementary Materials: Figure S1: $^1$H NMR spectra of 4. Figure S2: $^{13}$C NMR spectra of 4. Figure S3: HRMS (ESI) of 4.

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References


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