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Short Note

bis[*N*-(4-Bromophenyl)pyridine-2-carboxamidato]palladium

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Abstract: We report the crystal structure of *bis*[*N*-(4-bromophenyl)pyridine-2-carboxamidato]Palladium (**C1**) which was isolated from the reaction of aqueous potassium tetrachloropalladate(II) and *N*-(4-bromophenyl)-pyridine-2-carboxamide in dichloromethane under nitrogen flow. The structure was characterised by the following spectroscopic methods ^{1}H NMR, FT-IR and X-ray diffraction.

Keywords: Palladium(II) complex; bidentate pyridine amide ligand; carboxamide ligand

1. Introduction

The success of *cis*-diamminedichloro-platinum(II) (cisplatin) as an anticancer drug led to an increase in the synthesis and biological application of Pt-based anticancer agents [1–6]. Due to several side effects associated with the administration of cisplatin and Pt based anticancer agents such as nephrotoxicity to drug resistance of the tumour cells, researchers are exploring alternatives. One such alternate is the use of transition metal-based anticancer drugs [7–11]. Palladium-based complexes have gained significant attention due to their structural similarities, thermodynamics similarity and significant overlap of coordination chemistry to Pt(II) complexes. Pd(II) complexes exhibit promising activity towards cisplatin-resistant cells [12–14]. The coordination of biologically active molecules to metal centers shows promising activity due to the ability of the complexes to bind to different biological targets [15,16]. The incorporation of carboxamide groups in the ligands and preparation of new complexes allows for the unique effects of electronics and the steric effect control of the properties of the coordinated Pd(II) metal. The carboxamide ligand has a diverse chemistry due to its multifunction coordination modes [17–19]. As such, the *N*-(4-bromophenyl)-pyridine-2-carboxamide ligand, which acts as a bidentate-chelating ligand, was reacted with a Pd(II) metal precursor to form **C1** which forms a 2:1 complex with palladium(II). This paper reports the single-crystal structural data of *bis*[*N*-(4-bromophenyl)-pyridine-2-carboxamidato]Palladium and the other characterization data collected using various spectral techniques.

2. Results

In the subsequent Pd(II) complex, the *N*-(4-bromophenyl)-pyridine-2-carboxamide ligand acted as bidentate and was coordinated via anionic N_{amido} and neutral $N_{pyridine}$ sites via two five-membered chelate rings. In the ^{1}H NMR spectrum of **C1** (Figure S2, supplementary materials), the expected chemical shifts of the protons were observed and deshielded compared to the free ligand (Figure S1). The formation of the Pd(II) complex was revealed by the disappearance of the NH peak at 9.803 ppm in the ^{1}H NMR spectrum (Figure S1), which was attributed to the coordination of the Pd to the N_{amide}. The formation of **C1** was further confirmed using FT-IR, where the N–H stretches of the ligand at 3321 cm^{-1} (Figure S3) disappeared when compared to the FT-IR spectrum of **C1** (Figure S4). The FTIR spectra of the **C1** showed that the peaks for the C=O amide bands (1709 cm^{-1}) shifted when compared to the corresponding ligand (1673 cm^{-1}).

The molecular structure of **C1** was further confirmed by X-ray crystallography. **C1** was crystallized from the 1:1 dichloromethane and hexane solution to obtain crystals suitable for

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X-ray crystallography. The crystal structure of **C1** (Figure 1) assumes the distorted square-planar coordination geometry around the metal centre and belongs to the monoclinic system, with the space group P21/*c*. The *N*-(4-bromophenyl)-pyridine-2-carboxamide ligand binds to the palladium in a bidentate fashion, forming a two five-membered chelate ring through N-bonding of the $N_{pyridine}$ and N_{amide}. The selected bond lengths and bond angles of **C1** are represented in Table 1. **C1** adopts a distorted square-planar coordination geometry around the metal centre, with the angles N2–Pd1–N1, $N2^1$–Pd1–$N1^1$, N2–Pd1–$N1^1$ and $N2^1$–Pd1–N1 deviating by approximately 10° from the expected square-planar angle of 90°. The bond lengths reported in Table 1 indicate that the values relative to the pyridine N donors (Pd1-N1, Pd1-$N1^1$) are slightly longer by ca. 0.038 Å than those of the amide nitrogen atoms.

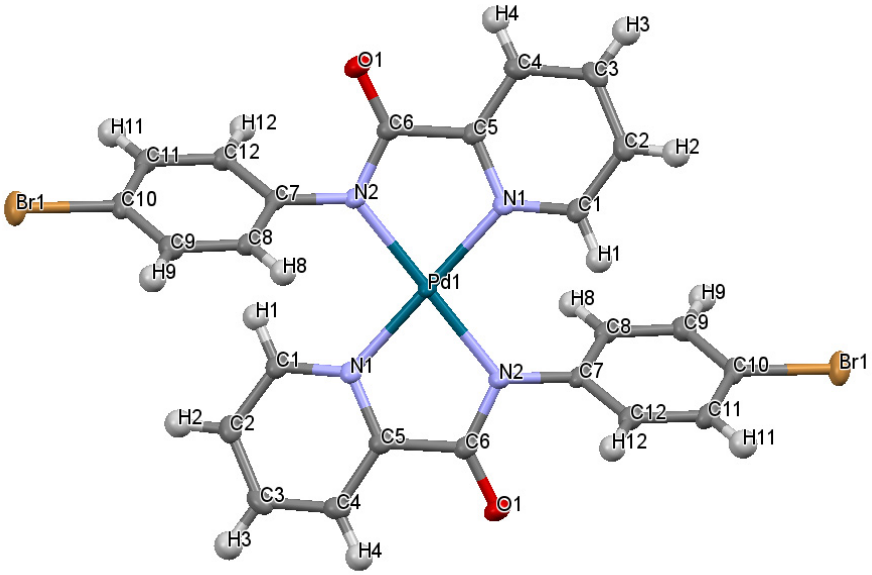


Figure 1. The ORTEP diagram of **C1** with the thermal ellipsoids drawn at the 50% probability level.

Table 1. Selected geometrical parameters for **C1**.

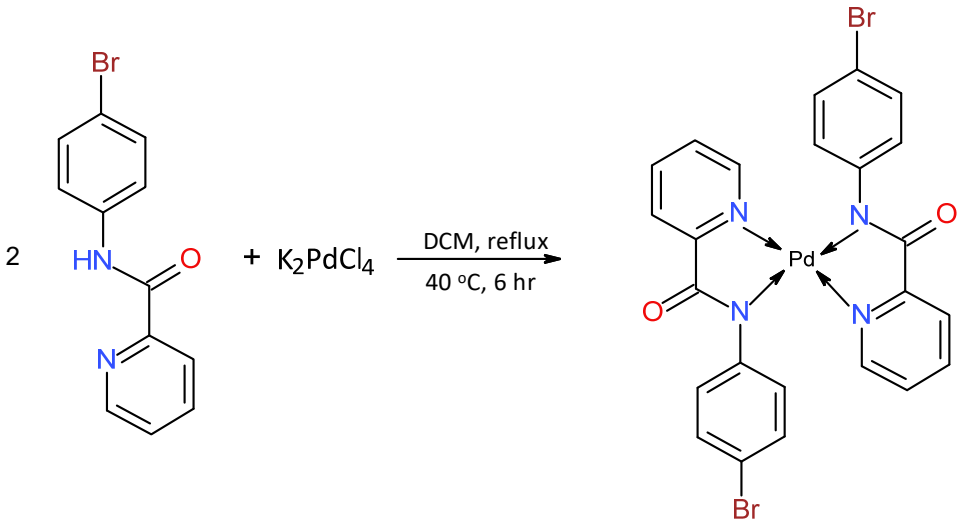
Atom	Length/Å	Atom	Angle/°
Pd1-$N2^1$	2.0361(19)	$N2^1$-Pd1-N2	180.0
Pd1-N2	2.0361(19)	N2-Pd1-N1	80.35(8)
Pd1-$N1^1$	2.0399(19)	$N2^1$-Pd1-$N1^1$	80.35(8)
Pd1-N1	2.0400(19)	N2-Pd1-$N1^1$	99.65(8)
		$N2^1$-Pd1-N1	99.65(8)
^{1}1-X, 1-Y, 1-Z		$N1^1$-Pd1-N1	180.0

3. Materials and Methods

All syntheses were performed under nitrogen using the standard Schlenk line techniques. Potassium tetrachloropalladate (98%) was purchased from Sigma-Aldrich and used without further purification. All solvents were procured from Sigma-Aldrich and were of analytical grade. ^{1}H NMR spectra were acquired on Bruker Avance III 400 MHz NMR spectroscopy with a 5 mm TBIZ probe at 30 °C. Chemical shifts were reported in ppm in relation to the solvent (acetone-d_6) residual peak, at 2.04 ppm. Coupling constants (J) were calculated in hertz (Hz). The infrared spectrum was recorded using a Bruker Alpha II FT-IR spectrometer and the data were reported as a percentage transmittance at the respective wavenumbers (cm^{-1}). Exemplary ^{1}H NMR and IR spectra of the ligand and **C1** are shown in Figures S1–S4, supplementary materials.

*3.1. Synthesis of bis[N-(4-bromophenyl)pyridine-2-carboxamidato]Palladium (**C1**)*

N-(phenyl) pyridine-2-carboxamide ligand (L1) was synthesized according to the standard literature methods [20,21]. Afterwards, L1 was coordinated to Pd(II) (Scheme 1) using a literature method [22]. An aqueous solution of potassium tetrachloropalladate (0.3063 mmol, 0.10 g) was added dropwise to a solution of the *N*-(phenyl) pyridine-2-carboxamide ligand (0.6127 mmol, 0.17 g) in DCM (10 mL). The mixture was stirred under reflux for 6 h and allowed to cool to room temperature. The precipitate that formed was filtered and washed with cold ultra-pure water and methanol. Yield: 0.085 g (42%), ^{1}H-NMR (400 MHz, CD_3COCD_3, ppm): 8.67 (d, *J* = 4.9 Hz, 2H, H_1-py), 8.23 (d, *J* = 7.2 Hz, 2H, H_4-py), 8.06 (td, *J* = 7.7 Hz, 2H, H_3-py), 7.93 (d, *J* = 8.8 Hz, 4H, H_5 and H_8), 7.64 (t, *J* = 6.4 Hz, 2H, H_2-py), 7.54 (d, *J* = 8.8 Hz, 4H, H_6 and H_7). FT-IR (cm^{-1}): 3001, 1709, 1357, 1217, 902, 525.



Scheme 1. Synthesis of the *bis*[*N*-(4-bromophenyl)pyridine-2-carboxamidato]Palladium complex.

3.2. X-ray Crystallography

The X-ray crystallographic data of **C1** were collected and evaluated on a Bruker APEX Duo [23] CCD area detector diffractometer with an Incoatec micro source working at 30 W power. The crystal was kept at 99.97 K during data collection using an Oxford Instruments Cryojet accessory. The data were collected with Cu(Kα), λ = 1.54178), at a crystal-to-detector distance of 50 mm. The SAINT [24] program was used to reduce the structure using the outlier rejection, scan speed scaling and the standard Lorentz and polarization correction factors. The non-hydrogen atoms were initially refined isotropically and then by anisotropic refinement with a full-matrix least-squares method based on F^2. All hydrogen atoms were included and positioned geometrically on their parent atoms. The crystal structure was solved with Olex2 [25], while the SHELXS [26] and SHELX [27] programs were used for structural refinement. The crystallographic data were visualized using WinGX [28] and Mercury v.4.3 [29]. The crystallographic data and structure refinement parameters of **C1** are given in Table 2.

Table 2. Crystal structure and structure refinement for **C1**.

Identification Code for C1	**cu_SS_PM_Br_Pd_Comp_0m**
Empirical formula	$C_{12}H_8BrN_2OPd_{0.5}$
Formula weight	329.31
Temperature (K)	99.97
Crystal system	monoclinic

Table 2. *Cont.*

Identification Code for C1	cu_SS_PM_Br_Pd_Comp_0m
Space group	$P2_1/c$
a (Å)	6.22590(10)
b/Å	12.9253(3)
c (Å)	13.6735(3)
α (°)	90
β (°)	94.8170(10)
γ (°)	90
Volume (Å^3)	1096.44(4)
Z	4
ρ_{calc} (g cm^{-3})	1.995
μ (mm^{-1})	11.358
F (000)	640.0
Crystal size (mm^3)	0.205 × 0.075 × 0.065
Radiation source, λ (Å)	Cu(K_α), λ = 1.54178
2θ range for data collection (°)	9.432 to 144.36
Index ranges	$-7 \leq h \leq 6$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$
Reflections collected	14,012
Independent reflections	2097 [R_{int} = 0.0247, R_σ = 0.0160]
Data/restraints/parameters	2097/0/151
Goodness-of-fit on F^2	1.125
Final R indexes [I >= 2σ (I)]	R_1 = 0.0213, wR_2 = 0.0513
Final R indexes (all data)	R_1 = 0.0216, wR_2 = 0.0515
Largest diff. peak/hole (e Å^{-3})	0.49/−0.79

4. Conclusions

bis[*N*-(4-bromophenyl)pyridine-2-carboxamidato]Palladium (**C1**) was synthesised and characterised by ^{1}H NMR and FT-IR spectroscopic techniques. The complex crystallizes in the monoclinic crystal system and in the P21/c space group. **C1** adopts the distorted square-planar coordination geometry around the metal centre.

Supplementary Materials: The following are available online. Figure S1: ^{1}H NMR spectrum of *N*-(4-bromophenyl)pyridine-2-carboxamide, Figure S2: ^{1}H NMR spectrum of *bis*[N-(4-bromophenyl)-pyridine-2-carboxamidato], Figure S3: IR spectrum of *N*-(4-bromophenyl)pyridine-2-carboxamide and Figure S4: IR spectrum of *bis*[*N*-(4-bromophenyl)pyridine-2-carboxamidato]Palladium (**C1**).

Author Contributions: T.R.P. conceived and designed the structure, revised the manuscript. P.N.M. completed the synthesis, crystal growth, partial characterisation. S.S. resourcing of synthesis, characterisation, reviewing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: CDCC No: 2215371 (**cu_SS_PM_Br_Pd_Comp_0m**) contains the supplementary crystallographic data for **C1**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (accessed on 1 November 2022), or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or via email: deposit@ccdc.cam.ac.uk.

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Conflicts of Interest: The authors declare no conflict of interests.

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