

КРАТКИЕ СООБЩЕНИЯ

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CHARACTERIZATION, CRYSTAL STRUCTURE DETERMINATION,
AND LUMINESCENT PROPERTIES OF [Pd(4,4'-bit)Cl₂]

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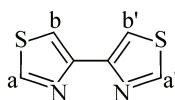
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Complex [Pd(4,4'-bit)Cl₂] (1) is synthesized by the reaction of PdCl₂ and 4,4'-bithiazole (4,4'-bit) in acetonitrile and crystallized by vapor diffusion of methanol into a dimethyl sulfoxide solution of the complex. This complex is thoroughly characterized by elemental analysis, IR, ¹H NMR, UV-Vis, and luminescence spectroscopy and its structure is studied by the single crystal X-ray diffraction method. The X-ray structure determination shows that in the structure of this complex, the Pd(II) atom is four-coordinated in a slightly distorted square-planar configuration by two nitrogen atoms from a bidentate 4,4'-bithiazole ligand and two chloride ions.

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Palladium(II) complexes containing bidentate N,N-donor ligands are important due to their application as catalysts [1–3], antibacterial [4, 5], antitumor [6, 7], and cytotoxic agents [8, 9]. Although the synthesis and characterization of the 4,4'-bithiazole compound was reported by Erlenmeyer and Ueberwasser in 1939 [10], and its crystal structure was determined by the X-ray diffraction method by Rae and coworkers in 1988 [11], but to the best of our knowledge, there are limited reports on the coordination compounds containing this ligand. 4,4'-Bithiazole (scheme) is a good bidentate N,N-donor ligand, and only few complexes with this ligand have been reported, such as that of gold [12], platinum [13], indium [14], iron [15–18], nickel [11], lead [19, 20], bismuth [21], and ruthenium [22]. All these complexes are fully characterized by spectroscopic methods and their structures were studied by the single crystal X-ray diffraction method. In continuation of these research works, herein we report the synthesis, characterization, and crystal structure of a new square planar palladium(II) complex with chloride and 4,4'-bithiazole.



4,4'-Bithiazole

Experimental. Materials and physical methods. 4,4'-Bithiazole was prepared according to the procedure described previously [10]. Other materials were purchased from Merck and used without further purification. IR spectra (4000–250 cm⁻¹) were obtained as CsI pellets using a Unicam Matson 1000 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker FT-NMR 500 MHz spectrometer using DMSO-*d*₆ as a solvent. The elemental analysis was performed using a Heraeus CHN-O

Table 1

IR frequencies of 4,4'-bit and complex **1** (cm⁻¹)

Compound	$\nu(\text{C—H})$	$\nu(\text{C=C}), \nu(\text{C=N}),$ $\nu(\text{C—C}), \nu(\text{C—N})$	$\nu(\text{C—S}), \delta(\text{C—N}),$ $\delta(\text{C—C}), \delta(\text{C—S})$	$\nu(\text{Pd—Cl})$	$\nu(\text{Pd—N})$
4,4'-bit	3125m, 3043m	1516w, 1434s, 1388m, 1296s, 1181m, 1035m	882s, 857s, 738m, 641m	—	—
[Pd(4,4'-bit)Cl ₂]	3081m, 3022m	1531m, 1444s, 1360s, 1310m, 1191m, 1058m	911m, 871m, 819s, 754m	340s, 306m	274m, 255m

Rapid analyzer. Melting point was obtained by a Kofler Heizbank Rechart type 7841 melting point apparatus. UV-Vis spectra were recorded on a Shimadzu 2100 spectrometer using a 1 cm path length cell in DMSO at room temperature, and luminescence spectra were recorded on Perkin Elmer LS 45 using a 1 cm path length cell.

Synthesis of [Pd(4,4'-bit)Cl₂] (1). A suspension of PdCl₂ (0.11 g, 0.62 mmol) in CH₃CN (60 ml) was stirred and warmed to 70 °C to give an orange solution. Then 4,4'-bithiazole (0.10 g, 0.62 mmol) in CH₃CN (20 ml) was added and the mixture was stirred at 70 °C for 5 min until a precipitate formed. The orange precipitate was filtered and dissolved in DMSO. Suitable crystals for the X-ray diffraction measurement were obtained by methanol diffusion into the orange solution of **1** in DMSO over four days (yield 0.16 g, 74.6 %, m.p. > 300 °C). Infrared frequencies (CsI, cm⁻¹) are reported in Table 1. ¹H NMR (DMSO-*d*₆, ppm) for the free 4,4'-bithiazole ligand: 8.06 (d, *J* = 2.1, 2H) and 9.20 (d, *J* = 2.1, 2H); for the complex: 8.36 (d, *J* = 1.8, 2H) and 9.41 (d, *J* = 1.8, 2H). UV-Vis: λ_{max} (DMSO, nm) for the free 4,4'-bithiazole ligand at 265 and for the complex at 263. Elemental analysis: C₆H₄Cl₂N₂PdS₂ (345.55); Anal. Calcd (%): C 20.85, H 1.16, N 8.10. Found: C 20.72, H 1.15, N 8.05.

Single crystal X-ray diffraction analysis. The X-ray diffraction measurements were made on a Bruker APEX II CCD area detector diffractometer with graphite monochromated MoK α radiation (λ = 0.71073 Å) at 298 K. The structure of **1** was solved by SHELX-97 and absorption correction was applied using the SADABS program [23]. Data collection, cell refinement, and data reduction were made using APEX II, SAINT, SHELXTL, PLATON, and MERCURY [23–26]. Crystal chemical information on the structure investigated was deposited with the Cambridge Structural Database under number CCDC 1444515, from where it can be obtained free of charge on request at the following website: www.ccdc.cam.ac.uk/products/csd/faqs.

Results and discussion. Synthesis of [Pd(4,4'-bit)Cl₂] (1). Complex **1** was obtained by the reaction of one equivalent of PdCl₂ with one equivalent of 4,4'-bithiazole in acetonitrile. Suitable crystals of the title complex were obtained for the X-ray diffraction measurement by methanol diffusion into a DMSO solution.

Spectroscopic characterization of [Pd(4,4'-bit)Cl₂] (1). The infrared spectra in Table 1 show the vibrational frequencies of the free 4,4'-bithiazole ligand and complex **1**. Two medium absorption bands in the range 3125–3022 cm⁻¹ for these compounds are assigned to the C—H stretching vibrations of the thiazole rings. In the infrared spectrum of the free 4,4'-bithiazole ligand, several bands observed in the range 1516–641 cm⁻¹ are assigned to C=N, C=C, C—C, C—N and C—S stretching vibrations and C—N, C—C and C—S bending vibrations [14, 15]. In the infrared spectrum of complex **1** these absorption bands are shifted to higher frequencies upon coordination. Similar shifts have been observed for bipyridine and 2,2'-dimethyl-4,4'-bithiazole ligands coordinated to metals as well [27–29] and can be explained by changing the geometry of the free ligand from *anti* to *syn* orientation in the coordinated case. The far IR spectrum of complex **1** was recorded between 400 and 250 cm⁻¹. The Pd—Cl stretching vibrations are seen at 340 and 306 cm⁻¹ and the Pd—N stretching vibrations are seen at 274 and 255 cm⁻¹ [30–32].

The electronic absorption spectra of the dimethyl sulfoxide solution of the free 4,4'-bithiazole ligand and complex **1** are shown in Fig. 1. As shown in this figure, the strong broad bands at around

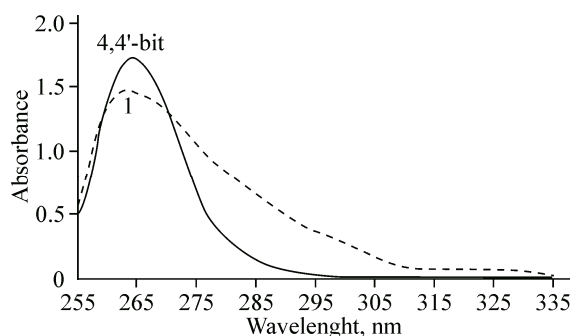


Fig. 1. Absorption spectra of 4,4'-bit (4×10^{-5} M) and **1** (3×10^{-5} M) in a DMSO solution at room temperature

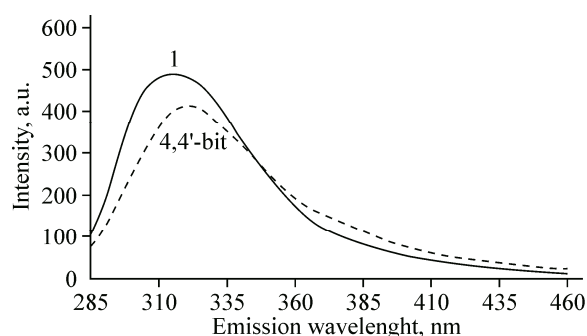


Fig. 2. Luminescence spectra of 4,4'-bit (4.18×10^{-4} M) and **1** (4.12×10^{-4} M) in DMSO at room temperature; excitation wavelength = 263 nm

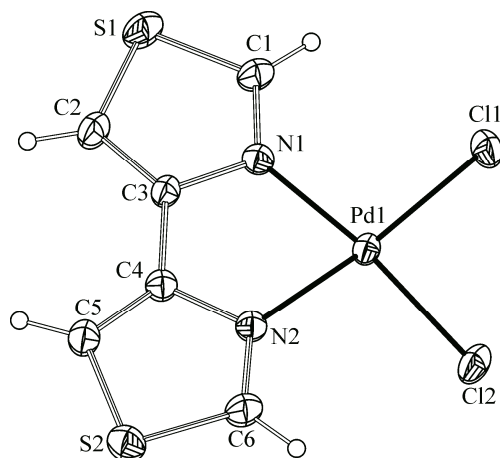
264 cm^{-1} for the free 4,4'-bithiazole ligand and complex **1** are assigned to the intraligand $\pi \rightarrow \pi^*$ transitions [14, 15].

The ^1H NMR spectra of the free 4,4'-bithiazole ligand and complex **1** were measured in a DMSO- d_6 solution at room temperature and the results are listed in the experimental section. The ^1H NMR spectrum of the free 4,4'-bithiazole ligand exhibited resonances at δ 8.06 (d, H_b and $\text{H}_{b'}$) ppm and 9.20 (d, H_a and $\text{H}_{a'}$) ppm. The ^1H NMR spectrum of complex **1** exhibited two sets of resonances at δ 8.36 (d, H_b , $\text{H}_{b'}$) ppm and 9.41 (d, H_a , $\text{H}_{a'}$) ppm. A comparison between the ^1H NMR spectra of the title complex and the free 4,4'-bithiazole ligand indicates that the protons of thiazole rings in the title complex shift downfield by $\Delta\delta = 0.30$ and 0.21 ppm with respect to the corresponding free 4,4'-bithiazole protons due to the inductive effect of the metal [33—35].

Luminescence emission spectra ($\lambda_{\text{ex}} = 263 \text{ nm}$) of the free 4,4'-bithiazole ligand and **1** were recorded in a DMSO solution at room temperature and the results are displayed in Fig. 2.

As shown in this figure, the 4,4'-bithiazole ligand and **1** exhibit broad luminescent emission centered at 322 and 315 nm, respectively. There is a shift (about 7 nm) of the emission energies of 4,4'-bithiazole after coordination to the Pd(II) cation in complex **1**. Also, the luminescent emission of complex **1** is stronger than that of the free bithiazole ligand. The shapes of the luminescence emission spectra of 4,4'-bithiazole and complex **1** are similar, therefore the emission properties of complex **1** are believed to have originated from $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transitions in the 4,4'-bithiazole ligand. The observed shift for **1** can be explained by a decrease in the energy gap between the ground and excited states in the 4,4'-bithiazole ligand upon complexation with Pd(II). The same trend is found for other complexes with different metal centers [14, 36—40].

Description of the molecular structure of [Pd(4,4'-bit)Cl₂] (1). Crystallographic data and selected bond lengths and angles for **1** are listed in Tables 2 and 3, respectively.



The X-ray crystallographic analysis shows that complex **1** crystallizes in the monoclinic crystal system with the $C2/m$ space group. The ORTEP view with the atom numbering scheme for this complex is shown in Fig. 3. As it is depicted in this figure, each Pd(II) cation is four-coordinated in a slightly distorted square-planar configuration by two nitrogen atoms from a bidentate 4,4'-bithiazole ligand and two terminal chloride ions. The main contribution to the distortion is the tight

Fig. 3. Molecular structure of [Pd(4,4'-bit)Cl₂] (**1**), with the atom numbering scheme and 30% probability displacement ellipsoids

Table 2

Crystallographic and structure refinement data for **1**

Parameter	Value
Formula	C ₆ H ₄ Cl ₂ N ₂ PdS ₂
Formula weight	345.55
Temperature, K	298(2)
Wavelength λ , Å	0.71073
Crystal System	Monoclinic
Space group	<i>C2/m</i>
<i>a</i> , <i>b</i> , <i>c</i> , Å	16.577(3), 6.8348(10), 8.7414(18)
β , deg.	94.749(16)
<i>V</i> , Å ³	987.0(3)
<i>Z</i>	4
ρ_{calc} , g/cm ³	2.326
μ , mm ⁻¹	2.793
<i>F</i> (000)	664
Crystal size, mm	0.25×0.20×0.18
Range of data collection over θ , deg.	2.47–27.00
Intervals of reflection indices	$-21 \leq h \leq 21$, $-8 \leq k \leq 8$, $-9 \leq l \leq 11$
Number of meas. / indep. reflections	3347 / 1166 ($R_{\text{int}} = 0.0841$)
Completeness over $\theta = 27.00$, %	99.5
<i>R</i> factors over $F^2 > 2\sigma(F^2)$	$R1 = 0.0359$, $wR2 = 0.0922$
<i>R</i> factors over all reflections	$R1 = 0.0406$, $wR2 = 0.0941$
<i>S</i>	1.077
Residual electron density (min / max), e/Å ³	1.409 / -1.631

Table 3

Bond distances (Å) and bond angles (deg.) for **1**

Pd1—N1	2.016(5)	N2—Pd1—N1	80.25(17)	N2—Pd1—Cl1	173.72(13)
Pd1—N2	2.005(4)	N2—Pd1—Cl2	92.43(13)	N1—Pd1—Cl1	93.47(13)
Pd1—Cl2	2.2944(14)	N1—Pd1—Cl2	172.68(13)	Cl2—Pd1—Cl1	93.85(6)
Pd1—Cl1	2.2964(14)				

N1—Pd1—N2 chelate angle (80.25(17)°), which results in the non-linear *trans* arrangement (N1—Pd1—Cl1 = 172.68(13)°). The Pd—N bond lengths are 2.005(4) and 2.016(5) Å and Pd—Cl bond lengths are 2.2944(14) Å and 2.2964(14) Å. The Pd—N and Pd—Cl bond lengths and angles (Table 3) are in good agreement with the corresponding values in [Pd(bipy)Cl₂] [41] and [PdCl₂{4,4'-(OH)₂-2,2'-bipy}] [42], (bipy is 2,2'-bipyridine and 4,4'-(OH)₂-2,2'-bipy is 4,4'-(OH)₂-2,2'-bipyridine).

In the crystal structure of **1**, there are S··S intermolecular contacts (Fig. 4), occurring between the S1 and S2 atoms of the thiazole rings from consecutive complexes with S1··S1ⁱⁱⁱ and S2··S2^{iv} distances of 3.538(2) Å and 3.591(3) Å respectively, which is shorter than the sum of the van der Waals radii of the two S atoms (3.7 Å) [Symmetry codes: ⁱⁱⁱ $-x, y, -1-z$ and ^{iv} $1-x, 1-y, -1-z$], intermolecular C—H··Cl hydrogen bonds (Table 4, Fig. 4) and short Pd··Pd intermolecular interactions along the crystallographic *b* axis between the two adjacent layers (Fig. 5), with a Pd1··Pd1ⁱ distance of 3.4722(7) Å [Symmetry code: ⁱ $1/2-x, 3/2-y, -z$] and Pd1··Pd1··Pd1 angle of 159.61(2)° [42]. These S··S and Pd··Pd interactions and also intermolecular C—H··Cl hydrogen bonds lead to the formation of a three-dimensional supramolecular network.

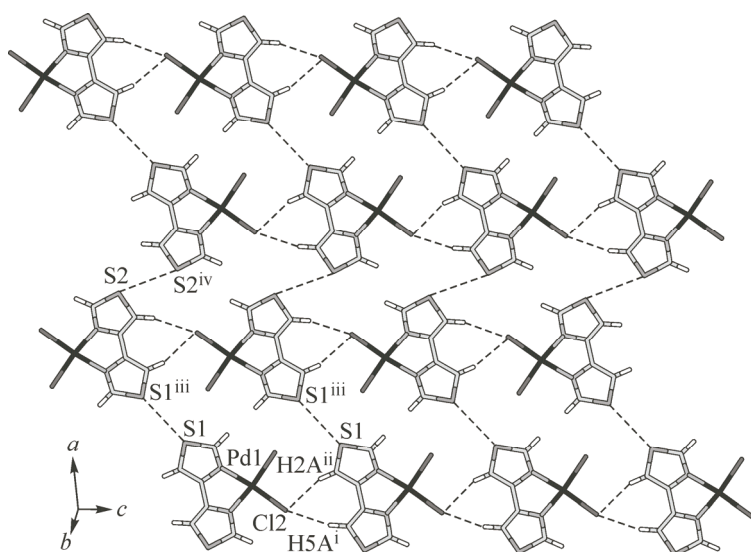


Fig. 4. View of the intermolecular C—H...Cl hydrogen bonds and S...S interactions present in the structure of complex **1**.

Symmetry codes: ⁱ $x, y, -1+z$; ⁱⁱ $x, 1-y, -1+z$; ⁱⁱⁱ $1-x, 1-y, -1-z$; ^{iv} $-x, y, -1-z$

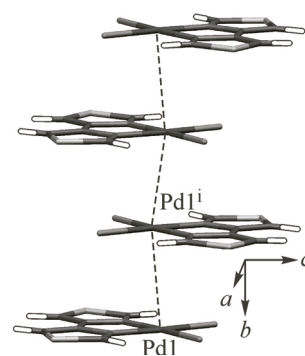


Fig. 5. Pd...Pd interactions within the layers of complex **1**.

Symmetry code: ⁱ $1/2-x, 3/2-y, -z$

Table 4

Hydrogen bond geometry for **1** in crystal packing (Å, deg.)

D—H...A	D—H	H...A	D...A	D—H...A
C2—H2A...Cl2 ^{#1}	0.9300	2.7700	3.660(6)	161.00
C5—H5A...Cl2 ^{#2}	0.9300	2.6600	3.567(5)	164.00

Symmetry operation: ^{#1} $x, 1-y, -1+z$; ^{#2} $x, y, -1+z$.

In this work, new complex [Pd(4,4'-bit)Cl₂] (**1**) have been synthesized. This complex was fully characterized by spectroscopic methods and its structure was determined by the single crystal X-ray diffraction method. In this complex, the Pd(II) atom is four-coordinated in a slightly distorted square planar geometry. It is notable that in this complex, the S...S intermolecular interactions, nonclassical C—H...Cl hydrogen bonds, and the Pd...Pd intermolecular interactions mostly stabilize the crystal lattice. Furthermore, the luminescence studies show differences in the luminescence behaviour of complex **1** in comparison with the free 4,4'-bithiazole ligand. Luminescence emission of complex **1** was shifted and stronger than that of the free 4,4'-bithiazole ligand.

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