

Synthesis, crystal structure, and analytical characterizations of amphiphilic palladium(II) compound containing bis(benzylthio)methylenepropanedioate

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(Received June 19, 2023; Revised August 1, 2023; Accepted August 2, 2023)

Abstract: The reaction of *cis*-protected (Me₄en)Pd(II) species with potentially multidentate bis(benzylthio)methylenepropanedioate (L) was carried out to obtain a monometallic compound, [(Me₄en)Pd(L)], in *O,O'*-coordination mode. The bis(benzylthio)methylene group was bent strikingly from the palladium square plane at the dihedral angle of 70.40°. The physicochemical properties of the present palladium(II) compound were fully characterized by means of infrared and nuclear magnetic resonance spectroscopy, thermogravimetric analysis, and single-crystal X-ray diffraction measurement.

Key words: coordination mode, crystal engineering, X-ray diffraction, NMR spectroscopy

1. Introduction

Research on systematic construction of novel coordination-driven transition-metal compounds is a fruitful field¹⁻⁷ for various task-specific applications such as gas sorption, recognition, catalysis, biomedicine, molecular separation, toxic-material adsorption, ion exchange, and luminescence sensing.⁸⁻¹³ Such designed coordination architectures have been widely synthesized according to the selection of basic molecular components such as the coordination geometry around the metal ions, the binding site, and the flexibility of ligands/co-ligands, counterions, and reaction solvents.¹⁴⁻¹⁸ In particular, many discrete palladium(II) complexes with multidentate ligands have contributed to the

development of coordination materials such as catalysts, rectangular building blocks, and morphology control.¹⁹⁻²⁵ Palladium(II) ions have been employed as useful angular directional units of square-planar geometry with the associative/dissociative dual characteristics by means of the labile Pd–N bond.^{26,27} Among various multidentate ligands, a series of bis(alkylthio)ylidenemalonate anionic ligands of appropriate flexibility can coordinate to metal ions via one of the three possible (*O,O'*)-, (*O,S*)-, or (*S,S'*)-modes, owing to factors such as co-ligands, solvent media, and temperature,²⁸ resulting in the formation of discrete compounds as well as coordination polymeric compounds.²⁹ In this context, reports on synthesis and structural behavior not only in the solid state but also

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in solutions of metal compounds containing bis(alkylthio)ylidenemalonate ligands have been published.³⁰ Herein we report the molecular structure of a monometallic palladium(II) compound constructed from the reaction of *cis*-protected (Me₄en)Pd(II) species with bis(benzylthio)methylenepropanedioate (**L**) ligand. Its characterizations by means of infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, thermogravimetric analysis (TGA), and single-crystal X-ray diffraction (SC-XRD) measurement also are reported in these pages.

2. Experimental

2.1. Chemicals and reagents

All of the reagents and solvents used in the present experiments were purchased from commercial sources and used without further purification. (Me₄en)PdCl₂¹⁹ and barium bis(benzylthio)methylenepropanedioate (Ba[**L**])³⁰ were prepared according to the procedures outlined in the literature. IR spectra were obtained on a Thermo Fisher Nicolet iS5 FT-IR spectrometer with samples prepared as KBr pellets. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded at ambient temperature on a Bruker Advance III HD 400 MHz FT-NMR spectrometer. Elemental microanalyses (C, H, N) were performed on samples in solid form using a Thermo Fisher Scientific IT/Flash 2000 installed at the Center for University-Wide Research Facilities (CURF) at Jeonbuk National University. Thermal analyses were performed under N₂ at a scan rate of 10 C/min using a Labsys TGA-DSC 1600.

2.2. Synthesis and crystallization

Silver sulfate (0.4 mmol, 0.124 g) in water (15 mL) was added to a suspension of (Me₄en)PdCl₂ (0.4 mmol, 0.117 g) in water (15 mL). The reaction mixture was stirred for 1 h, after which the silver chloride precipitate was filtered off. To this filtrate was added an aqueous suspension of Ba[**L**] (0.4 mmol, 0.198 g), and the reaction solution was stirred for 8 h at room temperature in darkness. After the barium

sulfate was filtered off, the filtrate was evaporated to dryness using a rotary evaporator at temperatures below 40 °C, thereby affording the yellow crystalline solid. Single crystals suitable for single-crystal X-ray diffraction analysis were formed in a mixture of chloroform and *n*-hexane to a 49 % yield (0.114 g). Mp: 158 °C (dec.). Anal. Calcd. for C₂₄H₃₀N₂O₄S₂Pd: C, 49.61; H, 5.20; N, 4.82. Found: C, 49.57; H, 5.23; N, 4.80. IR (KBr pellet, cm⁻¹): 3441, 2983, 2939, 1632, 1614, 1520, 1495, 1452, 1325, 1213, 1105, 1068, 984, 958, 814, 775, 700, 644, 609. ¹H NMR (400 MHz, CD₃OD, ppm): 7.49 (d, *J* = 7.6 Hz, 4H), 7.40 (t, *J* = 7.2 Hz, 4H), 7.28 (t, *J* = 7.2 Hz, 2H), 4.22 (s, 4H), 2.70 (s, 4H), 2.47 (s, 12H).

2.3. X-ray crystallography and structural determination

Standard solution: 100 mg of triflusal was dissolved in 20 mL mobile phase to obtain a 5000 µg/mL stock solution. This solution was diluted with mobile phase to prepare a 500 µg/mL standard solution. X-ray data for the present compound were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo K α (λ = 0.71073 Å) and a CCD detector at -25 °C. Forty-five frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for the Lorentz and polarization effects. The data reduction was performed using the Bruker APEXII with SADABS packages.³¹ The structure was solved by direct methods and refined by full-matrix least squares calculation using SHELX-2018/3.^{32,33} The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined only for the isotropic displacement parameters. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table 1. CCDC-2270024 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement for [(Me₄en)Pd(L)]

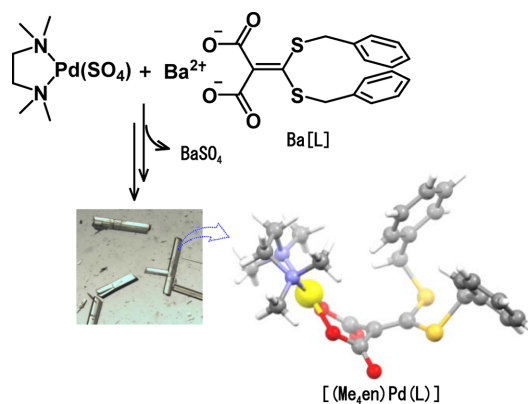
Empirical formula	C ₂₄ H ₃₀ N ₂ O ₄ S ₂ Pd
Weight (g mol ⁻¹)	581.02
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	
<i>a</i> (Å)	36.081(7)
<i>b</i> (Å)	8.299(2)
<i>c</i> (Å)	16.829(3)
<i>α</i> (°)	90
<i>β</i> (°)	95.19(3)
<i>γ</i> (°)	90
Volume (Å ³)	5018(2)
Z	8
Density (Mg m ⁻³)	1.538
Absorption coefficient (cm ⁻¹)	0.939
<i>F</i> (000)	2384
	44 ≤ <i>h</i> ≤ 44
Index ranges	10 ≤ <i>k</i> ≤ 10
	20 ≤ <i>l</i> ≤ 20
Reflections collected	19447
<i>R</i> _{int}	0.0370
Completeness to <i>θ</i> = 25.242° (%)	100.0
Data / restraints / parameters	4938 / 44 / 361
GoF on <i>F</i> ²	1.045
<i>R</i> ₁ ^a	0.0244
<i>wR</i> ₂ ^b	0.0661

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \frac{(\sum [w(F_o^2 - F_c^2)^2])^{1/2}}{(\sum [w(F_o^2)^2])^{1/2}}$$

3. Results and Discussion

3.1. Synthetic aspect

The present palladium(II) compound was synthesized by the reaction of *cis*-protected palladium(II) sulfate [(Me₄en)Pd(SO₄)], Me₄en = *N,N,N',N'*-tetramethylethylenediamine) with barium salt of bis(benzylthio) methylenepropanedioate (**L**) in water, and then was recrystallized in a mixture of chloroform and *n*-hexane to obtain pale-yellow crystalline products, [(Me₄en)Pd(L)] (Scheme 1). The products are soluble in water, methanol, ethanol, acetone, nitromethane, acetonitrile, chloroform, dimethyl sulfoxide (Me₂SO), and *N,N*-dimethylformamide, but are insoluble in *n*-hexane and diethyl ether. Even though the analogues with aliphatic moieties or cyclic chains were hardly



Scheme 1. Synthesis of [(Me₄en)Pd(L)].

soluble in chlorinated solvents such as chloroform and dichloromethane,³⁰ the present palladium(II) compound exhibited unprecedented amphiphilic properties that are soluble in aqueous media and organic solvents including chloroform, presumably owing to the presence of peripheral aromatic moieties. As depicted in Fig. S1, the ¹H NMR spectra were consistent with the proposed structure, indicating that [(Me₄en)Pd(L)] was inert even in polar solvents such as acetonitrile and dimethyl sulfoxide. In CD₃OD solution, the two singlets corresponding to methyl (CH₃) and methylene (CH₂) moieties of Me₄en co-ligand at 2.47 and 2.70 ppm, respectively, appeared. In addition, the resonances of **L** appeared as a singlet at 4.22 ppm and a multiplet at 7.49–7.28 ppm. As depicted in Fig. 1, the asymmetrical and symmetrical stretching frequencies of the carboxylate moiety of the product appeared at 1632 and 1325 cm⁻¹, respectively, unlike those (1591 and 1350 cm⁻¹) of **L**, indicating that complexation had been accomplished. According to the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) results, as depicted in Fig. S2, the present crystalline product has a reasonable degree of thermal stability in the solid state. The compound decomposes at around 160 °C, which is comparable to the formation of the thermodynamically favorable species. Its thermal decomposition in the 160–500 °C range corresponds to the weight loss of **L**, which can be attributed to the collapse of the skeleton. At above 500 °C, the crystals were finally changed to palladium(II) oxide residues.

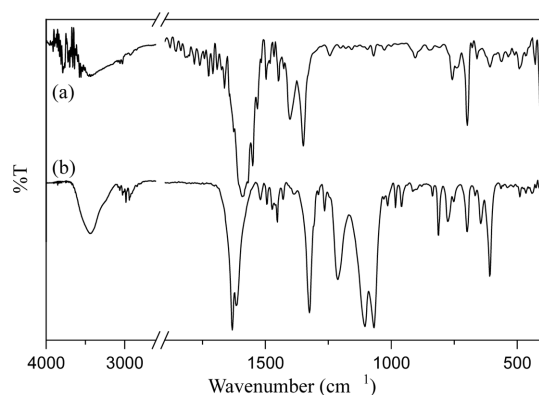


Fig. 1. IR spectra (KBr pellet) for Ba[L] (a) and [(Me₄en)Pd(L)] (b).

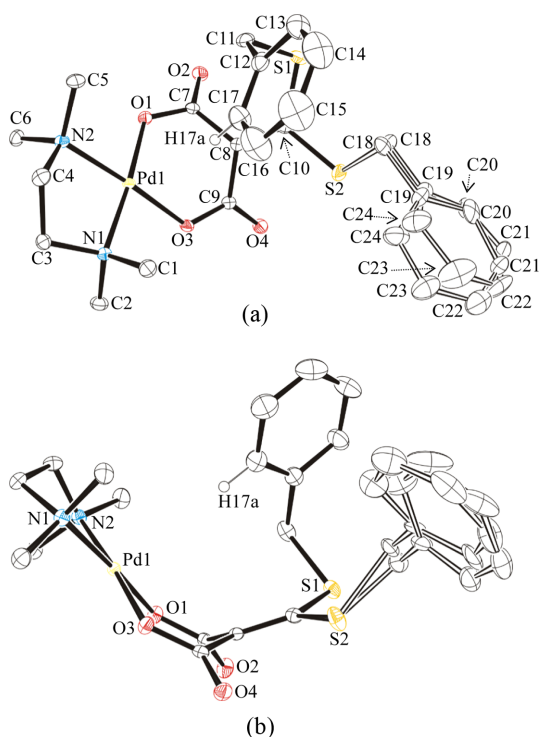


Fig. 2. ORTEP drawings of top (a) and side (b) views of [(Me₄en)Pd(L)] with anisotropic displacement parameters at 30% probability. All of the hydrogen atoms (except H17a) were omitted for clarity. One of the two benzylic groups is crystallographically disordered in a 0.5 : 0.5 occupancy.

3.2. X-ray crystal structure

The molecular structure of [(Me₄en)Pd(L)] is depicted in Figs. 2 and 3, and the relevant bond lengths and angles are listed in Table 2. In a crystallographic

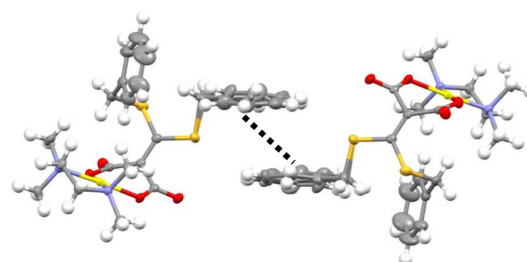


Fig. 3. Ball-and-stick drawing of [(Me₄en)Pd(L)] showing intermolecular $\pi \cdots \pi$ interaction.

Table 2. Selected bond lengths (Å) and angles (°) for [(Me₄en)Pd(L)]

Pd(1)–N(1)	2.046(2)
Pd(1)–N(2)	2.037(2)
Pd(1)–O(1)	2.007(2)
Pd(1)–O(3)	2.003(2)
O(1)–C(7)	1.301(3)
O(2)–C(7)	1.217(3)
O(3)–C(9)	1.293(3)
O(4)–C(9)	1.231(3)
C(7)–C(8)	1.518(3)
C(8)–C(9)	1.508(3)
C(8)–C(10)	1.346(4)
S(1)–C(10)	1.773(3)
S(2)–C(10)	1.770(3)
<hr/>	
N(1)–Pd(1)–N(2)	86.45(8)
O(1)–Pd(1)–O(3)	92.20(7)
N(1)–Pd(1)–O(1)	175.65(8)
N(2)–Pd(1)–O(3)	176.28(8)
C(7)–C(8)–C(9)	116.9(2)
S(1)–C(10)–S(2)	116.4(2)

asymmetric unit, there is one palladium(II) ion, one Me₄en, and one divalent anionic L. The X-ray crystallographic characterization of [(Me₄en)Pd(L)] revealed that the local geometry around the palladium(II) approximates to a square planar arrangement with two carboxylates in the *cis* position (Pd–O(1) = 2.007(2) Å; Pd–O(3) = 2.003(2) Å; O(1)–Pd–O(3) = 92.20(7)°). Concomitantly, the neutral Me₄en co-ligand is bonded to the palladium(II) ion in a *cis* bidentate fashion (Pd–N(1) = 2.046(2) Å; Pd–N(2) = 2.037(2) Å; N(1)–Pd–N(2) = 86.45(8)°). The intramolecular distance between the palladium(II) ion and the proton in an *ortho*-position of an aromatic ring (H17a) was

determined to be 3.046 Å in the solid state. The present anionic ligand is coordinated with palladium(II) in *O,O'*-fashion, similar to the methyl- and ethyl-analogues.³⁰ One of the two benzylic group is crystallographically disordered in a 0.5 : 0.5 occupancy. The intermolecular $\pi\cdots\pi$ interactions between the adjacent disordered aromatic benzylic moieties (3.65(9) Å; 0.0(2)°) exist in the solid state, as depicted in Fig. 3. The most interesting feature is that the bis(benzylthio) methylene group of the ligand is strikingly bent from the palladium square plane (the dihedral angle between the two planes = 70.40(6)°). Even though the ligand is an α,β -unsaturated carboxylic acid, the conformational bending prevents delocalization of its π electrons. As a proof of the localization, the bond length (1.346(4) Å) of the double bond C(8)–C(10) corresponds to that (1.34 Å) of a normal ethylene group.³⁴ The differences of bond lengths between palladium(II)-coordinated C–O (1.301(3) and 1.293(3) Å) and free C–O (1.217(3) and 1.231(3) Å) bonds is coincident with the localization. No other exceptional features, neither those of bond lengths nor angles, were observed.

4. Conclusions

We demonstrated the construction of an unprecedented amphiphilic monometallic palladium(II) compound containing a potential tetradentate bis(benzylthio)methylenepropanedioate ligand, and its crystal structure and physicochemical properties were fully characterized as well. The *O,O'*-bonding mode of the present **L** toward central palladium(II) ion was stable in the solid state as well as in the solution. More systematic studies, for example on the synthesis of bimetallic complexes through the *S,S'*-donating mode, are in progress. Further experiments, moreover, will provide more detailed information on the intriguing potentials of the complexes' catalytic and photoluminescence properties.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the

Korean Government (2018R1C1B6002006).

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