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Palladium(II) complexes of 1,10-phenanthroline: Synthesis and X-ray crystal structure determination

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Abstract

Two palladium(II) complexes, $[\text{Pd}(\text{phen})(\text{N}\equiv\text{CCH}_3)_2][\text{O}_3\text{SCF}_3]_2$ (**1**) and $[\text{Pd}(\text{phen})(\mu\text{-OH})_2][\text{O}_3\text{SCF}_3]_2 \cdot 2\text{H}_2\text{O}$ (**2**) (where phen = 1,10-phenanthroline), have been crystallized following the reaction of $\text{Pd}(\text{phen})\text{Cl}_2$ with silver triflate, $\text{Ag}(\text{O}_3\text{SCF}_3)$, in acetonitrile and water, respectively. The structures of both complexes are based on a $\text{Pd}(\text{phen})^{2+}$ metal core, with two acetonitrile molecules binding in a monodentate fashion in complex **1** and two hydroxo bridges holding together two cores to form a dimer in complex **2**. Additionally, both complexes present a hydrogen bonded 3-D network involving the triflate anions in **1**, and water and triflate anions in **2**. Both complexes have been characterized by infrared and ^1H NMR spectroscopy and their crystal structures determined by X-ray crystallography.

Keywords

Palladium; hydroxo dimer; phenanthroline; acetonitrile ligands

1. Introduction

Considerable effort has been directed to the study and understanding of the chemistry of palladium complexes due to their applications in catalysis [1], supramolecular chemistry [2] and medicine [3]. As part of these efforts, a few palladium(II) hydroxo-bridged dimers have been synthesized, characterized and their reactivity explored [4]. For example, Ruiz and coworkers have found that the reaction of hydroxo-bridged dimers of formula $[\text{Pd}_2(\text{C},\text{N})_2(\mu\text{-OH})_2]$ (where C,N = 2-(dimethylaminomethyl)phenyl or 2-(phenylazo)phenyl) with nitriles leads to the formation of the corresponding carboxamide complexes [5].

Although the chemistry of 2,2'-bipyridine, 1,10-phenanthroline and ethylenediammine palladium(II) complexes in aqueous media has been well investigated since the late 1980's [6–8], only a small number of complexes have been isolated and structurally characterized [9,10]. Just recently, the X-ray structure of $\text{Pd}(\text{en})(\text{NO}_3)_2$, a complex that has been used as a starting material in a myriad of reactions, has been determined [11]. Similarly, while there are

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4. Supplementary material

CCDC 649701 and 649702 contain the supplementary crystallographic data for complexes **1** and **2**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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a few examples of palladium(II) phenanthroline dimers with nitrogen and sulfur bridging ligands [12–14], there have not been any structural reports for hydroxide or alkoxide bridged complexes containing Pd(phen)^{2+} units.

With the above in mind, herein we report the synthesis, spectroscopic and structural characterization of two palladium(II) phenanthroline complexes, $[\text{Pd(phen)(N}\equiv\text{CCH}_3)_2][\text{O}_3\text{SCF}_3]_2$ (**1**), which provides an excellent source of Pd(phen)^{2+} for reactions in organic solvents, and $[\text{Pd(phen)(}\mu\text{-OH)}]_2[\text{O}_3\text{SCF}_3]_2\cdot 2\text{H}_2\text{O}$ (**2**), which, to the best of our knowledge, is the first palladium(II) phenanthroline di- μ -hydroxo dimer structurally characterized.

2. Experimental Section

2.1. Materials and Methods

Pd(phen)Cl_2 , where phen=1,10-phenanthroline, was synthesized according to literature [15]. Silver triflate, $\text{Ag}(\text{O}_3\text{SCF}_3)$, and potassium tetrachloropalladate(II), K_2PdCl_4 , were purchased from Sigma-Aldrich. 1,10-phenanthroline monohydrochloride was obtained from J. T. Baker. Deionized water ($18\text{ M}\Omega\text{ cm}^{-1}$) was obtained by passage of water through a Barnsted Nanopure system. Ether (ACS reagent grade) and CH_3CN (HPLC reagent grade) were obtained from Sigma-Aldrich and used without further purification. ^1H NMR spectra were recorded at 499.68 MHz on a Varian INOVA 500 MHz spectrometer. Chemical shifts for ^1H were referenced to the residual proton in the deuterated solvent (D_2O , 4.80 ppm; CD_3CN , 1.94 ppm). FT-IR spectra of solids were collected using a Bruker VECTOR 22 with an ATR attachment. Elemental analyses were performed by Midwest Microlab, LLC, Indianapolis IN.

2.2. Syntheses

2.2.1. $[\text{Pd(phen)(N}\equiv\text{CCH}_3)_2][\text{O}_3\text{SCF}_3]_2$ (1**)**—Complex **1** was prepared by adding $\text{Ag}(\text{O}_3\text{SCF}_3)$ (0.072 g, 0.28 mmol) to an acetonitrile suspension (80 ml) of Pd(phen)Cl_2 (0.050 g, 0.14 mmol). The mixture was heated with stirring at 65 °C for 2 hours and then filtered to remove AgCl . The resulting solution was dried by slow evaporation at 50 °C to obtain a yellow solid of **1**. X-ray diffraction quality crystals of complex **1** were obtained by vapor diffusion of ether over the resulting concentrated acetonitrile solution (0.027 g, 61 % yield). IR (cm^{-1} , solid): 3094 (w), 2995 (w), 2934 (w), 2341 (w), 2313 (w), 1585 (m), 1519 (m), 1429 (m), 1256 (s), 1222 (s), 1147 (s), 1030 (s), 851 (s), 710 (s). ^1H NMR (CD_3CN , δ in ppm): δ 9.37 (d, 1H); 8.90 (m, 2H), 8.84 (d, 1H), 8.19 (d, 2H), 8.01 (m, 2H). *Anal.* Calc for $[\text{Pd(phen)(N}\equiv\text{CCH}_3)_2][\text{O}_3\text{SCF}_3]_2\cdot 2\text{H}_2\text{O}$: C, 30.76; H, 2.58; N, 7.97; Found: C, 30.60; H, 1.86; N, 7.53.

2.2.2. $[\text{Pd(phen)(}\mu\text{-OH)}]_2[\text{O}_3\text{SCF}_3]_2\cdot 2\text{H}_2\text{O}$ (2**)**—Complex **2** was prepared by adding $\text{Ag}(\text{O}_3\text{SCF}_3)$ (0.0720 g, 0.280 mmol) to an aqueous suspension (100 ml) of Pd(phen)Cl_2 (0.050 g, 0.14 mmol). The mixture was heated with stirring at 65 °C for 12 hours and then filtered to remove AgCl . The resulting solution was concentrated to 5 ml by slow evaporation at 50 °C. As the solution cooled, light yellow, X-ray diffraction quality crystals of complex **2** formed (0.024 g, 37% yield). IR (solid, cm^{-1}): 3526 (w, br) 3442 (w, br), 3060 (m, br), 1607 (m), 1523 (m), 1434 (m), 1257 (s), 1220 (s), 1152 (s), 1026 (s), 854 (s), 713 (s). ^1H NMR (CD_3CN , δ in ppm): δ 9.38–7.51 (m, 16H). *Anal.* Calc for $[\text{Pd(phen)(}\mu\text{-OH)}]_2[\text{O}_3\text{SCF}_3]_2\cdot 2\text{H}_2\text{O}$: C, 33.17; H, 2.36; N, 5.95 Found: C, 33.40; H, 1.93; N, 5.87.

2.3. X-ray Crystallography

Selected crystallographic data and refinement details are given in Table 1. Intensity data for $[\text{Pd(phen)(N}\equiv\text{CCH}_3)_2][\text{O}_3\text{SCF}_3]_2$ (**1**) and $[\text{Pd(phen)(}\mu\text{-OH)}]_2[\text{O}_3\text{SCF}_3]_2\cdot 2\text{H}_2\text{O}$ (**2**) were measured on a Rigaku AFC12 κ /Saturn724 CCD fitted with Mo-K α radiation. The structures were solved by heavy-atom methods [16] and refinement was on F^2 [17], using data that had been corrected for absorption effects with an empirical procedure [18]. Non-hydrogen atoms

were modeled with anisotropic displacement parameters, with hydrogen atoms in their calculated positions. A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ was applied. Molecular structures, shown in Figs 1 and 3, were drawn at the 50% (**1**) and 70% (**2**) probability levels, respectively, using ORTEP [19]. The DIAMOND program [20] was used for the remaining figures. Data manipulation and analyses were performed with teXsan [21] and PLATON [22].

3. Results and discussion

3.1. Synthesis of palladium phenanthroline complexes

Reaction of Pd(phen)Cl₂ with Ag(O₃SCF₃) in acetonitrile led to the formation of complex **1**, while the same two reactants in water yielded complex **2**. In complex **1**, the chloride ligands were precipitated as AgCl leaving two open coordination places that were occupied by acetonitrile molecules. The reaction that gave complex **2** proceeded in a similar fashion, but in this case the species that was initially formed is believed to be the dication [Pd(phen)(OH₂)₂]²⁺ [7]. As the solution was slowly concentrated by evaporation of the water, the pH of the solution decreased from 3.12 after removal of the solid AgCl, to 2.56 at the point when complex **2** started to crystallize. Since no addition of base was necessary for the formation of the di- μ -hydroxo dimer, the hydroxo bridge was formed from water, leaving an excess of H⁺ in solution and making the aqueous solution more acidic. Complex **2** was not very soluble in water and precipitated as pale yellow crystalline needles. Similar behavior has been observed in the synthesis of the Pd dimer, [Pd(bipy)(μ -OH)]₂[NO₃]₂ (where bipy = 2,2'-bipyridine) [10].

The spectroscopic data obtained for complexes **1** and **2** are consistent with the proposed formula. The IR spectrum of solid **1** showed two bands at 2341 and 2313 cm⁻¹ due to the asymmetric and symmetric C $\equiv$ N stretching vibrations, respectively, of the coordinated acetonitrile molecules. As expected, coordination of the acetonitrile molecule to the palladium (II) metal center shifted these bands to higher wavenumbers from that observed for the non-coordinated acetonitrile (2295 (ν_{as}) and 2251(ν_s) cm⁻¹) due to back-bonding from the metal center. Comparable values have been reported in other complexes with coordinated acetonitriles [23]. The O-H stretching vibration of the bridging hydroxo groups of complex **2** appeared in the IR spectrum as a broad band at 3526 cm⁻¹. Additionally, another broad band at 3442 cm⁻¹ was also present due to non-coordinated water molecules, as observed in the X-ray crystal structure of **2**. Two bands corresponding to the triflate anions, at 1222 (ν_s CF₃) and 1030 (ν_s SO₃) cm⁻¹ for **1** and 1220 (ν_s CF₃) and 1026 (ν_s SO₃) cm⁻¹ for **2**, were present in the spectra of both complexes [24].

The ¹H NMR spectrum in CD₃CN of complexes **1** and **2** showed the signals for the protons of the phenanthroline rings in the aromatic region between 9.40 and 7.50 ppm. The ¹H NMR of complex **1** in D₂O showed an additional signal at 2.07 ppm corresponding to the acetonitrile molecules; this shift is very similar to the one reported for the free acetonitrile in D₂O (2.06 ppm) [25], so it is possible that in solution the acetonitrile molecules are substituted by D₂O molecules to yield [Pd(phen)(D₂O)₂](O₃SCF₃)₂. No signals were observed for the protons of the bridging hydroxo group in the ¹H NMR of complex **2** in either D₂O or CD₃CN. These protons have been observed before in other complexes by ¹H NMR with CDCl₃ as solvent [5,26]. Unfortunately, attempts to acquire the ¹H NMR spectra of complex **2** in CDCl₃ were unsuccessful due to its very low solubility.

3.2. Crystal structures analysis

3.2.1. [Pd(phen)(N $\equiv$ CCH₃)₂](O₃SCF₃)₂ (1**)**—The molecular structure of the dication in (**1**) is shown in Fig. 1 and selected bond lengths and angles are listed in Table 2; each of the

components of the structure has crystallographic mirror symmetry. In the dication, the mirror plane contains the Pd atom and bisects the 1,10-phenanthroline molecule. For each anion, the S and C atoms and one each of the O and F atoms lies on the mirror plane. The Pd atom exists within a strictly square planar geometry defined by a N₄ donor set, owing to symmetry. The Pd–N_{phen} and Pd–N_{acetonitrile} bond distances are equal within experimental error and deviations from the ideal square planar geometry are traced to the restricted bite distance of the 1,10-phenanthroline ligand. The structure reported here is isomorphous to that reported for the platinum analog [27] which displays similar structural characteristics with experimentally equivalent Pt–N bond distances. The crystal packing of (**1**) is dominated by $\pi\cdots\pi$ and C–H...O interactions, the latter are tabulated in Table 3. Dications pack into layers in the *ab*-plane and are stacked along the *c*-direction. Within layers, interactions are primarily of the type $\pi\cdots\pi$ where the peripheral edges of 1,10-phenanthroline are separated by approximately 3.6 Å. The coordinated acetonitrile molecules project externally to the layers, alternatively on either side, and their methyl-H atoms, as well as phenanthroline-H atoms, form a cooperative pattern of the C–H...O interactions with the triflate-O atoms resulting in a 3-D network, as illustrated in the crystal packing diagram of Fig. 2.

3.2.2. [Pd(phen)(μ -OH)]₂[O₃SCF₃]₂·2H₂O (2**)**—The structures of the centrosymmetric dication (**2**), the triflate anions and water molecules of crystallization, all connected by hydrogen-bonding are shown in Fig. 3. Selected bond lengths and angles are listed in Table 2. The central Pd atom exists within a N₂O₂ donor set that defines a square planar geometry. Deviations from the ideal geometry are related to the bonding requirements of the chelating ligand and the angle subtended at the Pd atom by the two hydroxyl groups. The dication is constructed about a centrosymmetric Pd₂O₂ core which takes the shape of a square as the Pd–O bond distances are equivalent within experimental error. The internal Pd...Pd distance is 3.0001(11) Å. The structure is isomorphous with the Pt analog [28], Pt...Pt is 3.0837(14) Å, and has the features reported recently for the 2,2'-bipyridine analog [Pd(bipy)(μ -OH)]₂[O₃SCF₃]₂ [10]. In the latter, the Pd–O bond distances of 2.0228(19) and 2.0195(19) Å are experimentally equivalent to those found for (**2**) as are the Pd–N distances. The crystal packing presents a myriad of hydrogen-bonding interactions involving all components of the crystal, Table 3. As can be appreciated from Fig. 3, the hydroxyl-H atoms are directed above and below the Pd₂O₂ core and each of these acts as a donor to a solvent water molecule. The latter forms two O–H...O hydrogen-bonds to two different triflate anions which in turn are connected to another water molecule so as to define a 12-membered [...HOH...OSO]₂ synthon with an extended chair conformation, Fig. 4. The resulting chains are orientated along the *b*-axis. Chains are connected with neighboring chains along the *c*-axis primarily via C–H...O contacts involving triflate-O atoms and connections along the *a*-axis, while also of the type C–H...O, involve both triflate-O as well as water-O atoms.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Molecular structure of the dication in $[\text{Pd}(\text{phen})(\text{N}\equiv\text{CCH}_3)_2][\text{O}_3\text{SCF}_3]_2$ (**1**) showing atomic labeling scheme. The molecule has crystallographically imposed mirror symmetry (symmetry operation *i*: $x, 1/2-y, z$) and the triflate anions are omitted.

Figure 2.
View of the crystal packing in $[\text{Pd}(\text{phen})(\text{N}\equiv\text{CCH}_3)_2][\text{O}_3\text{SCF}_3]_2$ (**1**) viewed down the a -axis showing C-H...O contacts as orange-dashed lines. Color code: Pd (orange), O (red), N (blue), C (grey), S (yellow), F (light blue) and H (green).

Figure 3.

Molecular structures of the components of $[\text{Pd}(\text{phen})(\mu\text{-OH})]_2[\text{O}_3\text{SCF}_3]_2 \cdot 2\text{H}_2\text{O}$ (**2**) showing atomic labeling scheme and hydrogen-bonding interactions (dashed lines) between them. Symmetry operation i : $-1-x, 1-y, -z$.

Figure 4.

View of the crystal packing in $[\text{Pd}(\text{phen})(\mu\text{-OH})]_2[\text{O}_3\text{SCF}_3]_2 \cdot 2\text{H}_2\text{O}$ (**2**) viewed down the a -axis showing O-H...O hydrogen-bonds as orange-dashed lines. Color code: Pd (orange), O (red), N (blue), C (grey), S (yellow), F (light blue) and H (green).

Table 1Crystallographic data for [Pd(phen)(N≡CCH₃)₂][O₃SCF₃]₂ (**1**) and [Pd(phen)(μ-OH)]₂[O₃SCF₃]₂·2H₂O (**2**)

	1	2
Formula	C ₁₈ H ₁₄ F ₆ N ₄ O ₆ PdS ₂	C ₂₆ H ₂₂ F ₆ N ₄ O ₁₀ Pd ₂ S ₂
<i>M</i>	666.85	941.40
<i>T</i> /K	173	93
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> -1
<i>a</i> /Å	9.5006(19)	7.0366(14)
<i>b</i> /Å	12.177(2)	9.6314(19)
<i>c</i> /Å	10.565(2)	12.492(3)
<i>α</i> /°	90	72.72(3)
<i>β</i> /°	107.04(3)	86.27(3)
<i>γ</i> /°	90	74.61(3)
<i>V</i> /Å ³	1168.6(4)	779.3(3)
<i>Z</i>	2	1 (dimer)
<i>d</i> _{calc} /g cm ⁻³	1.895	2.006
No. of unique reflns	2508	3196
No. of obsd reflns with <i>I</i> > 2σ(<i>I</i>)	2332	2945
<i>R</i> (<i>I</i> ≥ 2σ(<i>I</i>))	0.052	0.043
<i>a</i> , <i>b</i> for weighting scheme	0.019, 2.217	0.034, 0.972
<i>wR</i> (all data)	0.092	0.089
Max. and min. residuals, eÅ ⁻³	0.45, −0.77	0.80, −0.78

Table 2
 Selected bond lengths (Å) and angles (°) for complexes [Pd(phen)(N≡CCH₃)₂]
 [O₃SCF₃]₂ (**1**) and [Pd(phen)(μ-OH)]₂[O₃SCF₃]₂·2H₂O (**2**)

1			
Pd–N1	2.006(3)	Pd–N2	2.002(3)
N1–Pd–N2	176.62(13)	N1–Pd–N1 ⁱ	82.33(18)
N1–Pd–N2 ⁱ	94.31(13)	N2–Pd–N2 ⁱ	89.04(19)
2			
Pd–N1	1.995(3)	Pd–N2	2.001(3)
Pd–O1	2.013(3)	Pd–O1 ⁱ	2.016(3)
O1–Pd–N1	179.08(13)	O1–Pd–N2	96.72(13)
O1–Pd–O1 ⁱ	83.74(13)	N1–Pd–N2	82.44(14)
N1–Pd–O1 ⁱ	97.10(13)	N2–Pd–O1 ⁱ	179.37(12)

Table 3

Hydrogen-bonding parameters and other intermolecular interactions (A–H...B; Å, °) for [Pd(phen)(N≡CCH₃)₂][O₃SCF₃]₂ (1) and [Pd(phen)(μ-OH)]₂[O₃SCF₃]₂·2H₂O (2)

A	H	B	H...B	A...B	A–H...B	Symmetry operation
1						
C3	H3	O1	2.50	3.430(5)	176	$x, 1/2-y, z$
C6	H6	O1	2.51	3.366(5)	152	$1-x, 1/2+y, 2-z$
C2	H2	O3	2.50	3.245(5)	137	x, y, z
C1	H1	O4	2.57	3.443(5)	157	$x, 1/2-y, z$
C8	H8c	O4	2.45	3.139(5)	129	$x, 1+y, z$
2						
O1	H1o	O5	1.85	2.694(4)	179	x, y, z
O5	H1w	O3	2.01	2.849(4)	174	$-x, -y, -z$
O5	H2w	O4	1.98	2.821(4)	177	x, y, z
C3	H3	O4	2.41	3.362(5)	177	$x, 1+y, -1+z$
C5	H5	O2	2.49	3.430(6)	168	$x, 1+y, -1+z$
C6	H6	O2	2.56	3.414(6)	150	$1-x, -y, -z$
C9	H9	O5	2.45	3.203(5)	136	$1+x, y, z$