



Synthesis and structures of a palladium macrocycle, a six-membered palladacycle, and a palladium compartment complexes: $[\text{Pd}(\text{L}^1)\text{Cl}]$, $[\text{Pd}(\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)\text{Cl}_2]$, and $[\text{Pd}(\text{L}^2)]$ ($\text{HL}^1 = (E)\text{-}2\text{-}(((3\text{-aminopropyl})\text{imino})\text{methyl})\text{-}6\text{-methoxyphenol}$; $\text{H}_2\text{L}^2 = N,N'\text{-bis}(3\text{-methoxysalicylideneimino})\text{-}1,3\text{-diaminopropane}$)



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ARTICLE INFO

Article history:

Received 15 July 2016

Accepted 22 August 2016

Available online 31 August 2016

Keywords:

Palladium compartment complex

Schiff-base ligand

Crystal structures

Thermal conversion

Cyclohexane-like palladacycle

ABSTRACT

The Pd(II) bis(benzonitrile) complex $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ reacted with a mixture of 2-hydroxy-3-methoxybenzaldehyde, 1,3-diaminopropane, and triethylamine in acetonitrile to produce $[\text{Pd}(\text{L}^1)\text{Cl}]$ ($\text{HL}^1 = (E)\text{-}2\text{-}(((3\text{-aminopropyl})\text{imino})\text{methyl})\text{-}6\text{-methoxyphenol}$) (**1**), which contains an imine-amine-type macrocyclic ligand and a chloro ligand. Complex **1** was converted into a cyclohexane-like palladacycle, $[\text{Pd}(\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)\text{Cl}_2]$ (**2**), when heated in acetonitrile at 80 °C for 60 h. The palladium compartment complex $[\text{Pd}(\text{L}^2)]$ ($\text{H}_2\text{L}^2 = N,N'\text{-bis}(3\text{-methoxysalicylideneimino})\text{-}1,3\text{-diaminopropane}$) (**3**) was obtained from the free bis(imine) ligand (H_2L^2) and $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ or $\text{Pd}(\text{OAc})_2$ in methanol. All complexes were structurally characterized by X-ray diffraction. Complex **3** is the first structurally characterized palladium compartment complex, in which the compartment ligand has an inner N_2O_2 and an outer $\text{O}_2\text{O}'_2$ compartments. The coordination geometry of the palladium metal in all complexes (**1–3**) can be best described as square-planar.

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1. Introduction

Numerous coordination polymers (CPs) are currently designed and their properties are investigated thoroughly, due to their interesting topologies and useful applications such as energy transfer, magnetism, solid-state luminescence, biomedicine, catalysis, conductivity, host-guest, and so on [1–7]. Proper linking ligands, symmetrical or asymmetrical, are of fundamental importance for the preparation of desired CPs, and representative ligands are those containing pyridyl-pyridyl, amine-amine, carboxylate-carboxylate, thiophene-thiophene, or pyridyl-carboxylate terminals.

Secondary building units (SBUs) are stereochemically well-defined molecular complexes or metal clusters, and have been continually employed for the synthesis of CPs [8–11] and zeolites [12–14]. Compartmental Schiff-base ligands, acyclic or cyclic, and their metal complexes have continuously gained high attention [15,16]. In particular, several compartment complexes of *d*-block metals, which are combinations of *d*-block metals and

compartment ligands with an inner N_2O_2 and an outer $\text{O}_2\text{O}'_2$ compartments, have been utilized as SBUs to synthesize binuclear complexes (*3d–3d'*, *3d–3d''*, *3d–4f*) and multinuclear CPs, which are mainly used for the investigation of their magnetic properties [17–29]. Such compartment complexes are typically prepared from an aldehyde (or a ketone), a diamine, and a *d*-block metal by Schiff-base condensation with the aid of the template effects, and the metal is bound to the N_2O_2 donors.

Our group previously prepared several Ni–Ln CPs by treating the nickel compartment complexes (SBUs) with *f*-block metal nitrates in the presence of pyridyl-carboxylate-type linking ligands: (i) one-dimensional Ni–Ln CPs, $[\text{NiLn}(\text{L}^2)(\text{NO}_3)_2(4\text{-pyp})(\text{EtOH})]$ (Ln = Nd, Eu; 4-Hpyp = 4-pyridinepropionic acid) [30] and (ii) two-dimensional Ni–Ln CPs, $[\text{NiLn}(\text{L}^2)(\text{NO}_3)_2(4\text{-pca})(\text{H}_2\text{O})]$ (Ln = Nd, Eu, Tb; 4-Hpca = pyridine-4-carboxylic acid) [31] (for ligands, see Chart 1). Interestingly, we recently observed that the binuclear Ni–Ln (Nd, Tb) compartment complexes are thermally transformed into one-dimensional CPs in the absence of the external linking ligand: $[\text{Ni}_2\text{Nd}_2(\text{L}^2)_2(\text{H}_2\text{O})_2(\mu\text{-NO}_3)_3](\text{OH}^-)_3 \cdot 6\text{H}_2\text{O}$ and $[\text{Ni}_2\text{Tb}_2(\text{L}^2)_2(\mu\text{-NO}_3)_3(\text{H}_2\text{O})_2](\text{OH}^-)_3 \cdot 4\text{H}_2\text{O}$ [32].

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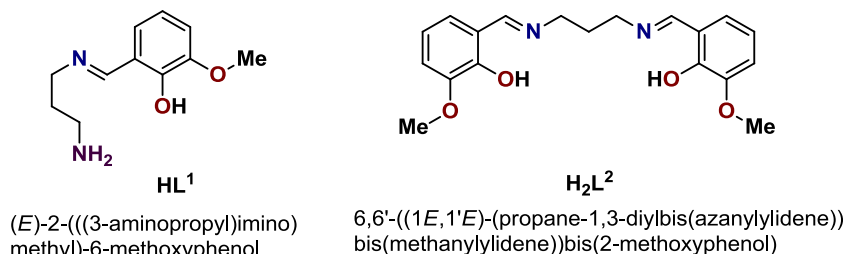


Chart 1. Ligands used in this study.

It is worth mentioning that almost all known compartment complexes of *d*-block metals include the first-row metals of groups 5–12, especially Co, Ni, Cu, and Zn [15–19]. However, there is a single case in the literature, in which the palladium metal (second-row metal) is coordinated to the compartment ligand (H_2L' : *N,N'*-bis(3-methoxysalicylideneimino)-1,3-diaminoethane) to form $[PdL']$. This complex was reported to be prepared by refluxing an ethanol solution of $PdCl_2$, 3-methoxysalicylaldehyde, and ethylenediamine with the help of template effects, without any spectral and structural data [33].

In this work, we made initial attempts to prepare palladium–lanthanide (4*d*–4*f*) CPs. For this purpose, a mixture of 2-hydroxy-3-methoxybenzaldehyde (or *ortho*-vanillin), $[Pd(PhCN)_2Cl_2]$, lanthanide nitrate, 1,3-diaminopropane, and triethylamine was stirred in acetonitrile. However, the product turned out to be $[Pd((3-OCH_3)-2-O-C_6H_3CH=NCH_2CH_2CH_2NH_2)Cl]$ (**1**), which contains an imine–amine-type ligand, not a compartment ligand (a bis(imine) ligand). Complex **1** was thermally converted into $[Pd(NH_2CH_2CH_2CH_2NH_2)_2Cl_2]$, dichloro(1,3-diaminopropane)palladium(II) (**2**). Our target palladium compartment complex, $[Pd(L^2)]$, could be prepared by treating the free Schiff-base ligand, *N,N'*-bis(3-methoxysalicylideneimino)-1,3-diaminopropane (H_2L^2), with $[Pd(PhCN)_2Cl_2]$ or $Pd(OAc)_2$. In this paper, we report the preparation and structures of complexes **1–3**.

2. Experimental

All solid reagents were purified by recrystallization, and all solvents were distilled and stored under argon. IR spectra were obtained in the range of 400–4000 cm^{-1} on a Vertex 70 FTIR spectrophotometer. For microwave-heating experiments, a microwave reactor Anton Paar (No.80868835, 300 W) was used. Elemental analyses were carried out by means of an Elementar Vario EL cube at the Cooperative Center for Research Facilities (CCRF) in Sungkyunkwan University. The free bis(imine) ligand (H_2L^2) was prepared by slightly modifying the literature method [34,35].

2.1. Preparation of $[Pd(L^1)Cl]$ ($HL^1 = (E)$ -2-(((3-aminopropyl)imino)methyl)-6-methoxyphenol) (**1**)

At room temperature, a mixture of 2-hydroxy-3-methoxybenzaldehyde (*ortho*-vanillin, 153 mg, 1.01 mmol), triethylamine (0.14 ml, 1.00 mmol), and 1,3-diaminopropane (0.08 ml, 0.9 mmol) was stirred in acetonitrile (5 ml) for 30 min. *trans*- $[Pd(PhCN)_2Cl_2]$ (384 mg, 1 mmol) was subsequently added, and the resulting mixture was stirred for 1 h. The resultant solution was filtered to give yellow-orange precipitate, which was filtered, washed with acetonitrile (2×2 ml), and then dried under vacuum to give the product (338 mg, 0.957 mmol). High-quality crystals were obtained by microwave heating (300 W) complex **1** (10 mg, 0.03 mmol) in acetonitrile (20 ml) at 80 °C for 2 h. The filtrated solution was allowed to evaporate slowly to give brown crystals (4.6 mg, 0.013 mmol, Yield: 46.0%). IR (KBr, cm^{-1}): 739, 862, 1333, 1447, 1613 (C=N),

3247 (N–H), 3280 (N–H). Mp: 160–161 °C. *Anal. Calc.* for $C_{11}H_{15}ClN_2O_2Pd$: C, 37.84; H, 4.33; N, 8.02. Found: C, 37.20; H, 4.71; N, 8.18%.

2.2. Thermal conversion of complex **1** to $[Pd(NH_2CH_2CH_2CH_2NH_2)_2Cl_2]$, dichloro(1,3-diaminopropane)palladium(II) (**2**)

An acetonitrile (20 ml) solution containing complex **1** (10 mg, 0.029 mmol) was heated in a Teflon-lined autoclave for 60 h at 80 °C, and then air-cooled slowly to room temperature for 24 h. The resulting brown crystals were filtered and air-dried to give complex **2** (brown crystals, 1.6 mg, 0.0064 mmol, Yield: 22.0%). IR (KBr, cm^{-1}): 739, 946, 1334, 1452, 1611, 3191 (N–H), 3271 (N–H). Mp: 199–201 °C.

2.3. Preparation of the free ligand (H_2L^2)

0.413 ml (4.95 mmol) of 1,3-diaminopropane was added slowly to 20 ml of a dry methanol solution containing 1.502 g (9.87 mmol) of *o*-vanillin. The resulting solution was refluxed at 80 °C for 1 h. Several spheres of zeolite 3A were added to the resulting deep transparent orange solution to remove water formed during the reaction, and yellow crystals appeared instantly. The crystals were filtered, washed with cold ethanol (3×3 ml), and then air-dried to give the yellow crystals (1.407 g, 4.11 mmol, Yield: 83.0%). IR (KBr, cm^{-1}): 837, 961, 1081, 1255, 1469, 1631 (C=N); mp: 97–98 °C. The identity and structure of the ligand was confirmed definitely by single crystal X-ray crystallography [35].

2.4. Preparation of $[Pd(L^2)](H_2O)(CH_3OH)$ (**3**·(H_2O)·(CH_3OH))

A methanol (5 ml) solution of the ligand (H_2L^2 , 0.085 g, 0.248 mmol) was added dropwise to a warm (50 °C) methanol (5 ml) solution of $Pd(OAc)_2$ (0.056 g, 0.249 mmol) under argon. The reaction mixture was refluxed at 80 °C for 2 h. The resulting orange precipitates were filtered and vacuum-dried to give complex **3**·(H_2O)·(CH_3OH) (92 mg, 0.185 mmol, Yield: 74.7%); IR (KBr, cm^{-1}): 741, 1078, 1225, 1317, 1469, 1624 (C=N). Mp: 190–192 °C (decom.). *Anal. Calc.* for $C_{20}H_{26}N_2O_6Pd$: C, 48.35; H, 5.27; N, 5.63. Found: C, 48.48; H, 4.68; N, 5.42%. Complex **3** was microwave-heated (300 W) in acetonitrile at 80 °C (stirring speed of 500 rpm) for 30 min, and the resulting solution was left for 3 days to evaporate slowly to give crystals for X-ray diffraction study.

2.5. X-ray structure determination

All X-ray data were collected at 296 K with a Bruker Smart APEX2 diffractometer (CCRF) equipped with a Mo X-ray tube. Collected data were corrected for absorption with SADABS based on the Laue symmetry by using equivalent reflections [36]. All calculations were carried out with SHELXTL programs [37]. Details on crystal data, intensity collection, and refinement details are given in

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