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Twisted dinuclear Pd(II) complex with an exo-hexadentate ligand bearing bipyridine and carbamoly groups: Synthesis and structure

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Abstract

Dinuclear Pd(II) compound, $[Pd_2(PMCB^{2-})Cl_2] \cdot CH_2Cl_2$ (**1**), has been prepared by the reaction of $K_2[PdCl_4]$ with exo-hexadentate ligand having amide groups (3,3′-bis[*N*-(2-pyridylmethyl)carbamoly]-2,2′-bipyridine, H_2PMCB) in H_2O/CH_2Cl_2. X-ray crystal structure of **1** indicates that one $PMCB^{2-}$ ligand binds two Pd(II) ions each having a distorted square planar structure. The bipyridine group of the $PMCB^{2-}$ ligand is involved in offset face-to-face π–π interactions, which gives rise to a 1D chain. The 1D chains are linked together via the C–H···O hydrogen bondings between a carbon atom of pyridine group and the oxygen of carbamoly group to generate a 2D network. Between the 2D networks there exist the herringbone π–π stackings, which results in a 3D supramolecular structure.

Keywords: Exo-hexadentate ligand; Dinuclear palladium(II) complex; Crystal structure; Hydrogen bonding; Offset π–π interaction

Transition metal complexes have been attracting considerable interest as these compounds have been utilized in catalysis and molecular magnetism as well as model compounds of metalloenzymes [1]. Among them, Pd(II) compounds have been extensively studied in catalysis involving C–H activation [2] and hydrolysis of peptides [3]. In particular, dinuclear complexes were found to be more effective than mononuclear ones in catalysis, i.e. hydrolysis of phosphate ester, because each metal ion cooperatively participates in substrate binding and activation [4]. However, the use of dinuclear Pd(II) complexes as catalysts has been limited [5], even though many monomeric Pd(II) compounds have been exploited to date [6]. Furthermore, noncovalent interactions such as π–π stacking and hydrogen bonding are employed to induce intermolecular interactions in supramolecular chemistry [7]. Such interactions are of great importance due to the various applications to molecular recognition in biological systems [8] and crystal engineering in supramolecules [9].

To prepare dinuclear Pd(II) complexes with potentially catalytic properties and induced intermolecular interactions to form supramolecules, exo-hexadentate ligand 3,3′-bis[*N*-(2-pyridylmethyl)carbamoly]-2,2′-bipyridine (H_2PMCB) was targeted. Herein, we report the synthesis and structure of novel ligand (H_2PMCB) and its Pd(II) dinuclear complex $[Pd_2(PMCB^{2-})Cl_2] \cdot CH_2Cl_2$ (**1**) towards this goal.

Targeted ligand (H_2PMCB) was obtained as a pale yellow solid by the treatment of thionyl chloride with 2, 2′-bipyridyl-3,3′-dicarboxlic acid followed by a reaction with 2-(aminomethyl)pyridine in CH_2Cl_2 as described in Scheme 1 [10]. H_2PMCB was clearly characterized by infrared and NMR spectroscopies. The infrared spectrum (KBr

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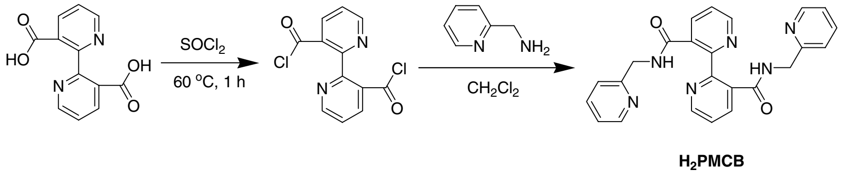

Scheme 1. Synthesis of targeted ligand (H_2PMCB).

pellet) of H_2PMCB shows ν_{NH} of the secondary amines at 3331 cm^{-1} and ν_{CO} of the amide groups at 1650 cm^{-1}. The ^1H NMR spectrum ($CDCl_3$) of the ligand exhibits 14 hydrogen atoms of pyridine groups in the range of 8.58–7.26 ppm, four hydrogens of two methylene groups at 4.51 ppm, and two hydrogen atoms of NH groups at 4.83 ppm. The ligand can be twisted due to the steric hindrance of functional groups attached at 3,3′-positions of bipyridine. That is, both pyridylmethyl groups are positioned toward the outside indicating that the ligand can be potentially coordinated to two metal ions to form dinuclear complexes and may also result in intermolecular interactions, i.e. π–π interactions (pyridine group) and hydrogen bonding (amide group). The reaction of two equivalents of $K_2[PdCl_4]$ with H_2PMCB and triethylamine in CH_2Cl_2/H_2O under aerobic conditions affords the expected air stable dinuclear complex $[Pd_2(PMCB^{2-})Cl_2] \cdot CH_2Cl_2$ (**1**) [11]. The composition of **1** was determined by elemental analysis, infrared, and X-ray diffraction. The IR spectrum of **1** (KBr pellet) had peaks characteristic of coordinated $PMCB^{2-}$ dianion due to the disappearance of secondary NH peak and the blue shift of ν_{CO} band. The IR spectrum of **1** showed strong absorptions at 1582 and 1553 cm^{-1} that are assigned to the uncoordinated CO vibrations of the amide groups, and the bands at 3073 and 2924 cm^{-1} are consistent with the C–H stretching frequencies of the $PMCB^{2-}$ ligand.

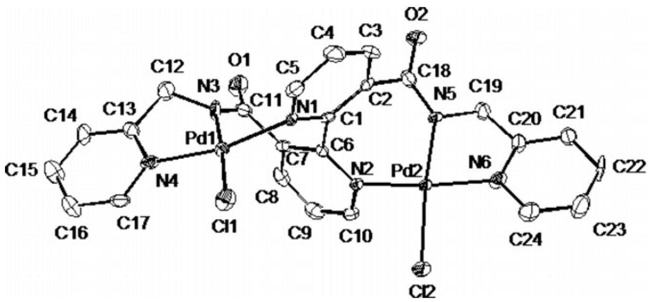

Fig. 1. Structure of the neutral Pd(II) dimer $[Pd_2(PMCB^{2-})Cl_2]$ in crystals of **1**. The atoms are represented by 50% probable thermal ellipsoid. Hydrogen atoms and solvent are omitted for clarity. Relevant distances (Å) and angles (°): Pd1–N1 2.033(6), Pd1–N3 1.950(7), Pd1–N4 2.010(7), Pd1–Cl1 2.322(2), Pd2–N2 2.034(7), Pd2–N5 1.967(6), Pd2–N6 1.997(7), Pd2–Cl2 2.319(2), O1–C11 1.242(10), O2–C18 1.241(10), N3–C11 1.336(12), N3–C12 1.457(11), N5–C18 1.328(11), N5–C19 1.462(11), C1–C6 1.513(12), C2–C18 1.527(12), C7–C11 1.522(11), C12–C13 1.512(12), C19–C20 1.509(11), N1–Pd1–N3 89.4(3), N1–Pd1–N4 166.8(2), N3–Pd1–N4 80.6(3), N1–Pd1–Cl1 93.70(19), N3–Pd1–Cl1 176.7(2), N4–Pd1–Cl1 96.2(2), N2–Pd2–N5 91.6(3), N2–Pd2–N6 167.1(3), N5–Pd2–N6 80.0(3), N2–Pd2–Cl2 92.54(19), N5–Pd2–Cl2 173.6(2), N6–Pd2–Cl2 95.0(2).

Yellow plate-shaped crystals of **1** suitable for X-ray diffraction were obtained by layering of an aqueous solution of $K_2[PdCl_4]$ into a dichloromethane solution of H_2PMCB. **1** crystallizes in the monoclinic $P2_1/c$ space group, and the atom labeling ORTEP drawing of **1** is shown in Fig. 1 [12]. The core structure of **1** is composed of one $[Pd_2(PMCB^{2-})Cl_2]$ dimer and one molecule of CH_2Cl_2 as lattice solvent. The structure of the Pd dimer displays a distorted square planar geometry by coordination of two nitrogen atoms from the pyridine and bipyridine groups, one nitrogen of amide moiety and a chloride ion. The average Pd–N_{amide}, Pd–$N_{pyridine}$, and Pd–Cl bond distances are 1.960(5), 2.020(3), and 2.321(1) Å, respectively. As expected, the Pd–N_{amide} distance is shorter than that of Pd–$N_{pyridine}$ (ca. 0.060 Å), indicating that N_{amide} ligand is stronger σ donor than $N_{pyridine}$ ligand. The Pd–Cl bond distances are similar to those reported for other compounds including Pd–Cl bonds [13]. Additionally, the average CO bond distance (1.242(7) Å) in deprotonated (amidate) groups is very close to that of protonated one (1.235(3) Å), showing that the COs of the amidate groups remain double bonds and are not delocalized [14]. The palladium ions are 0.084(3) and 0.131(3) Å out of the N_3Cl coordination plane for Pd1 and Pd2, respectively. The shortest Pd···Pd separation within the dimer is 5.736(1) Å and is ca. 2% greater than the shortest interdimer Pd···Pd distance of 5.631(1) Å. The bipyridine unit is not planar since the dihedral angle between the pyridine rings is 64.6(3)°. Such distortion is common and has been observed with other complexes bridged by a ligand containing 2,2′-bipy or 4,4′-bipy unit [15].

The bipyridyl group of **1** is involved in extensive π–π stacking interactions, such as offset face-to-face π–π interactions, between the pyridyl groups [16]. The pyridine group containing N1 located in the dimer undergoes this offset face-to-face π–π interaction with the N2(x, $-y+0.5$, $z-0.5$) of the pyridine group and is positioned at the neighboring dimer. The inter-planar separation of the pyridine rings is 3.49 to 3.65 Å (centroid···centroid, 3.918 Å) and the dihedral angle between the pyridine ring planes is 3.34°. Due to these π–π interactions **1** has a 1D chain structure (Fig. 2). Interestingly, intermolecular C–H···O hydrogen bonding interactions exist between the oxygen atom of amide moiety and a carbon atom of terminal pyridine ring belonging to the adjacent Pd(II) ion linking the 1D polymer into a 2D network O1···C21($-x+1$, $y+0.5$, $-z+1.5$) = 3.285(11) Å, ∠O1–H21–O21 = 154.60°; O2···C14($-x+1$, $y-0.5$, $-z+1.5$) = 3.412(11) Å,