



Syntheses, crystal structures and copper-binding capabilities of amidate-hanging platinum mononuclear complexes containing alkylamine moieties



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ARTICLE INFO

Article history:

Received 1 August 2013

Accepted 19 September 2013

Available online 14 October 2013

Keywords:

Platinum

Crystal structure

Alkyl

Hydrophobic

Multinuclear complex

ABSTRACT

As analogs of *cis*-[Pt(piam)₂(NH₃)₂]-2H₂O (**1**, piam = pivalamidate), two kinds of platinum mononuclear complexes, *cis*-[Pt(piam)₂(NH₂C₃H₇)₂]-H₂O (**2**) and *cis*-[Pt(piam)₂(NH₂C₄H₉)₂] (**3**), have been synthesized and characterized by single-crystal X-ray analyses. The square-planar complexes **2** and **3** contain propyl and butyl moieties, respectively, enhancing the hydrophobicity. Both compounds have non-coordinated oxygen atoms in the piam ligands that can bind to a second metal, such as the Cu²⁺ ion, to afford trinuclear Pt–Cu–Pt complexes. UV–Vis and electron paramagnetic resonance spectra of the reaction of **2** and **3** with the Cu²⁺ ion show that both compounds form dinuclear Pt–Cu complexes as intermediates.

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1. Introduction

Extensive recent research into the design and synthesis of multinuclear complexes has provided a wide variety of structures [1–20]. Among them, heterometallic cluster complexes with metal–metal bonds are of particular importance because the cooperative redox on the metals plays an essential role in unique electron transfers and characteristic magnetisms [6–20]. For rational synthesis of Pt heterometal linear complexes, “amidate-hanging” Pt mononuclear complexes are suitable starting materials, because they can readily bind to a second metal ion with the non-coordinated oxygen atoms of the amidate moieties [16,21,22]. The mononuclear amidate complexes are prepared by utilizing direct base hydrolysis of the corresponding nitrile complexes [6,23–28]. Although these “amidate-hanging” Pt mononuclear complexes are potential modules for obtaining multinuclear linear complexes, only a few examples have been reported [22,29]. In this paper, we report the syntheses and crystal structures of two novel compounds containing relatively long alkyl amines (Scheme 1), *cis*-[Pt(piam)₂(NH₂C₃H₇)₂]-H₂O (**2**, piam = pivalamidate) and *cis*-[Pt(piam)₂(NH₂C₄H₉)₂] (**3**), showing the second metal's binding capability.

2. Experimental

2.1. Materials

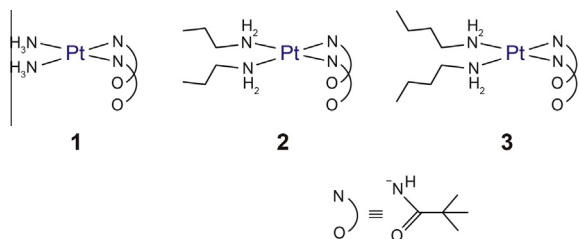
Potassium tetrachloroplatinate(II) was obtained from Tanaka Kikinzoku Co. NH₂C₄H₉, NaClO₄, CuCl₂·2H₂O and KI were obtained from Nacalai Tesque Co. Pivalonitrile and NH₂C₃H₇ were obtained from Tokyo Chemical Industry Co. AgNO₃ was obtained from Wako Co. *Cis*-[PtI₂(NH₂C₃H₇)₂] and *cis*-[PtI₂(NH₂C₄H₉)₂] were synthesized by a modification of Dhara's method [30,31].

2.2. Synthesis of *cis*-[Pt(piam)₂(NH₂C₃H₇)₂]-H₂O (**2**)

An aqueous solution (4 mL) of K₂PtCl₄ (0.42 g, 1.0 mmol) was stirred with KI (0.68 g, 4.1 mmol) for 15 min at 40 °C, and then NH₂C₃H₇ (0.38 mL, 4.6 mmol) was added. After stirring for 1 day, a yellow powder of *cis*-[PtI₂(NH₂C₃H₇)₂] was obtained. An aqueous solution (10 mL) of the yellow powder was stirred with AgNO₃ (0.34 g, 2.0 mmol) overnight in the dark, and AgI was then removed by filtration. The colorless filtrate was stirred with pivalonitrile (0.44 mL, 4.1 mmol) for 2 h, and then stirred for 1 day after addition of NaClO₄ (0.5 g, 4.1 mmol). The resulting white powder (0.41 g) was recrystallized from the mixed solution of Me₂CO (5 mL) and 1.0 M NaOH aqueous solution (10 mL) to obtain white crystals (0.19 g, 0.36 mmol) of *cis*-[Pt(piam)₂(NH₂C₃H₇)₂]-H₂O. Yield 36%. Elemental analysis calcd for C₁₆H₄₀N₄O₃Pt: C, 36.15; H, 7.58; N, 10.54, found: C, 36.35; H, 7.18; N, 10.54%.

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Scheme 1. Three kinds of amidate-hanging Pt mononuclear complex.

2.3. Synthesis of *cis*-[Pt(piam)₂(NH₂C₄H₉)₂] (**3**)

An aqueous solution (4 mL) of K₂PtCl₄ (0.42 g, 1.0 mmol) was stirred with KI (0.68 g, 4.1 mmol) for 15 min at 40 °C, and then NH₂C₄H₉ (0.45 mL, 4.5 mmol) was added. After stirring for 1 day, a yellow powder was obtained. An aqueous solution (10 mL) of the yellow powder was stirred with AgNO₃ (0.34 g, 2.0 mmol) overnight in the dark, and AgI was then removed by filtration. The colorless filtrate was stirred with pivalonitrile (0.44 mL, 4.1 mmol) for 4 h, and then stirred for 4 h after addition of NaClO₄ (0.5 g, 4.1 mmol). The resulting white powder (0.30 g) was recrystallized from the mixed solution of MeCN (1.5 mL) and 1.0 M NaOH aqueous solution (3 mL) to obtain a white powder. The white powder was recrystallized again from a mixed solution of Me₂CO (7 mL) and H₂O (7 mL) to obtain *cis*-[Pt(piam)₂(NH₂C₄H₉)₂] (85 mg, 0.16 mmol). Yield 16%. Elemental analysis calcd for C₁₈H₄₂N₄O₂Pt: C, 39.92; H, 7.82; N, 10.34, found: C, 39.29; H, 7.83; N, 10.17%.

2.4. Synthesis of [Pt₂Cu(piam)₄(NH₂C₄H₉)₄](PF₆)₂ (**4**)

A MeOH solution (8 mL) of CuCl₂·2H₂O (6.8 mg, 0.04 mmol) and **3** (65 mg, 0.12 mmol) was stirred for several minutes and mixed with an aqueous solution (0.5 mL) of NaPF₆ (25 mg, 0.15 mmol) at room temperature. After several days, light green crystals of [Pt₂Cu(piam)₄(NH₂C₄H₉)₄](PF₆)₂ were collected by filtration, washed with water and dried in vacuo (25 mg, 17 μmol). Yield 44%. Elemental analysis calcd for C₃₆H₈₄CuF₁₂N₈O₄P₂Pt₂: C, 30.10; H, 5.89; N, 7.80, found: C, 30.38; H, 6.01; N, 7.92%.

2.5. X-ray structure determination

Single crystals of **2**, **3** and **4** were mounted on a glass fiber and coated with epoxy resin. For each compound, X-ray data collection was carried out on a Rigaku AFC7R Mercury CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71070 Å) radiation, operated at 15 kW power (50 kV, 300 mA). A total of 744 frames were collected using a scan width of 0.5° with an exposure time of 5 s/frame. Empirical absorption corrections [32] were performed for all data. The structures were solved by the direct method [33] with subsequent difference Fourier syntheses and refinement with SHELX-97 [34], operated by the YADOKARI-XG software package [35]. The crystal data and the details of the structure determination are summarized in Table 1. The non-hydrogen atoms were refined anisotropically and hydrogen atoms, except for the ones in the water molecule, were treated as riding atoms. Selected bond lengths and angles are shown in Table 2.

2.6. Physical measurements

The IR spectra were recorded on a Perkin Elmer Spectrum 400 over the range 400–4000 cm⁻¹ at room temperature. UV–Vis spectra were recorded on a Shimadzu UV-3100PC over the range 340–1400 nm at room temperature. EPR spectra were measured

on a JEOL TE-200 spectrometer. The field sweep was monitored with an Echo Electronics EFM-2000 ¹H NMR gaussmeter, the probe of which was attached beside the EPR cavity.

3. Results and discussion

3.1. Synthetic procedure

Taking advantage of a similar base-hydrolysis method as for *cis*-[Pt(piam)₂(NH₃)₂]·2H₂O (**1**) [22], we tried to obtain the desired compounds. However, it was not successful because their precursors, *cis*-[Pt(NC^tBu)₂(NH₂C₃H₇)₂](ClO₄)₂ and *cis*-[Pt(NC^tBu)₂(NH₂C₄H₉)₂](ClO₄)₂, do not dissolve in H₂O. This insolubility in H₂O is attributed to the hydrophobic alkyl chains on the amine moieties. For both compounds, the addition of organic solvents (Me₂CO or MeCN) accelerated the base hydrolysis to afford *cis*-[Pt(piam)₂(NH₂C₃H₇)₂]·H₂O (**2**) and *cis*-[Pt(piam)₂(NH₂C₄H₉)₂] (**3**), where the C≡N stretching bands in the IR spectra, 2306 and 2234 cm⁻¹ for *cis*-[Pt(NC^tBu)₂(NH₂C₃H₇)₂](ClO₄)₂, 2303 and 2234 cm⁻¹ for *cis*-[Pt(NC^tBu)₂(NH₂C₄H₉)₂](ClO₄)₂, disappeared (Fig. 1). In addition, the intense bands for the ClO₄⁻ ions in the IR spectra also disappeared, indicating that the positive charges of Pt²⁺ are compensated with negative charges on the piam ligands. As mentioned below, both **2** and **3** reacted with the Cu²⁺ ion to afford trinuclear Pt–Cu–Pt complexes in MeOH. However, only crystals of [Pt₂Cu(piam)₄(NH₂C₄H₉)₄](PF₆)₂ (**4**) were obtained by the addition of an aqueous NaPF₆ solution to the MeOH solution.

3.2. Crystal structure of *cis*-[Pt(piam)₂(NH₂C₃H₇)₂]·H₂O (**2**)

Fig. 2 shows the crystal structure of **2**. The square-planar coordination geometry around the Pt atom consists of two *cis* N atoms of propylamine and two *cis* N atoms of the piam ligands. The sum of the four *cis* N–Pt–N angles is 360.1°, which is indicative of their coplanarity. The C(1)=O(1) (1.271(5) Å) and C(6)=O(2) (1.260(5) Å) bond lengths are in agreement with double-bond character. On the other hand, the C(1)–N(3) (1.291(5) Å) and C(6)–N(4) (1.307(5) Å) bond distances are shorter than the usual C–N single bond distance, indicating a partial double-bond character. The bond distances and angles are essentially the same as those reported for **1** [22]. The crystal contains water molecules, which are hydrogen bonded to the oxygen atoms in the piam ligands with distances of 2.828(7) and 2.876(6) Å (Fig. 2b). An interesting feature of the crystal packing is that two complex molecules stack in a face-to-face fashion with eight hydrogen bonds between the amine moieties and oxygen atoms in the piam ligands, where the Pt–Pt distance is relatively short (3.4913(6) Å). The propyl moieties have different conformations with N(1)–C(11)–C(12)–C(13) and N(2)–C(14)–C(15)–C(16) torsion angles of 179.87(6) and 67.86(9)°, respectively.

3.3. Crystal structure of *cis*-[Pt(piam)₂(NH₂C₄H₉)₂] (**3**)

Fig. 3 shows the crystal structure of **3**. Compound **3** also has a square-planar coordination geometry around the Pt atom, consisting of two *cis* N atoms of butylamine and two *cis* N atoms of the piam ligands. The bond lengths in the amidate moieties are similar to those in **2**; C(1)=O(1) = 1.237(5) Å, C(6)=O(2) = 1.245(5) Å, C(1)–N(3) = 1.318(5) Å and C(6)–N(4) = 1.319(5) Å, which indicate double-bond character between the C and O atoms. Compound **3** crystallizes without solvent molecules. The butylamines groups hydrogen bond to oxygen atoms in the piam ligands on either side of the complex, resulting in a one-dimensional alignment (Fig. 3b).

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