

## КРАТКИЕ СООБЩЕНИЯ

UDK 548.736

## CRYSTAL STRUCTURE OF DIAMMINE(MALONATO)PALLADIUM(II)

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Received September, 5, 2010

Diammine(malonato)palladium(II) is synthesized by the reaction of  $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$  with malonic acid, and its crystal structure is determined by single crystal X-ray diffraction. Distorted coordination square of the Pd(II) atom is formed by two N atoms of two ammonia molecules and two O atoms of bidentate malonate ligand. The average Pd—N and Pd—O distances are 2.018(7) Å and 2.014(2) Å, respectively. The molecules are stacked in such a way that the planes of coordination squares are parallel with the Pd···Pd distances between the nearest neighbors in a stack of 4.039 Å.

**Key words:** palladium, malonate, ammonia, crystal structure, synthesis.

Since the serendipitous discovery of the antitumor activity of cisplatin, *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, much effort has been focused on modifying this basic structural unit in order to develop more efficient and less toxic analogues [ 1—4 ]. Complexes with chelating carboxylates such as malonate (mal) as the leaving ligand are much less toxic than the chloride complexes [ 4—6 ]. The complex *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>(mal) demonstrated good activity against many tumors [ 7—8 ], and its crystal structure was also reported [ 9 ]. Because of similar coordination modes and chemical properties of palladium(II) and platinum(II), the anticancer activity of palladium complexes also drawn attention [ 10 ]. However, as compared to the systematic study of *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>(mal), less information is available about the corresponding palladium complex, *cis*-Pd(NH<sub>3</sub>)<sub>2</sub>(mal) [ 11 ]. In the present paper, we report the synthesis and crystal structure of *cis*-Pd(NH<sub>3</sub>)<sub>2</sub>(mal).

**Experimental. Synthesis.** Malonic acid (102 mg, 1.0 mmol) was added to a solution of  $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$  (298 mg, 1.0 mmol) in 10 ml of water. The solution was allowed to stand at room temperature to give yellow crystals. The crystals were washed with cold water and dried in vacuo. The yield was almost quantitative.

**X-ray diffraction analysis.** Intensity data for a single crystal (size 0.21×0.14×0.10 mm) was collected at room temperature on a BRUKER SMART APEX II equipped with a CCD detector using graphite-monochromated MoK<sub>α</sub> radiation ( $\lambda = 0.071073$  nm) in the  $\theta$  range from 2.30° to 28.23°. In total, 4380 reflections were measured. Crystallographic data:  $a = 4.0391(4)$  Å,  $b = 14.1750(13)$  Å,  $c = 11.3797(10)$  Å,  $\beta = 94.0200(10)^\circ$ , space group  $P2_1/c$ ,  $V = 649.93(10)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calcd}} = 2.478$  g/cm<sup>3</sup>. The crystal structure was solved by the direct method. The crystalline phase has the composition Pd(NH<sub>3</sub>)<sub>2</sub>(O(O)CCH<sub>2</sub>C(O)O). Final full-matrix refinement on 1527 independent reflections led to  $R1 = 0.0211$  ( $wR2 = 0.0472$ ). For 1381 reflections with  $I > 2\sigma(I)$ :  $R1 = 0.0181$  ( $wR2 = 0.0460$ ). The  $S$ -factor against  $F^2$  is 1.031. All calculations were made using the SHELXTL-97 software [ 12, 13 ]. The CIF file with complete information about the structure was deposited at CCDC (No. 761983),

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Table 1

*Bond Lengths (d, Å), Bond Angles (ω, deg.) for cis-Pd(NH<sub>3</sub>)<sub>2</sub>(mal)*

Bond	d	Bond	d	Angle	ω	Angle	ω
Pd(1)—N(2)	2.011(2)	O(1)—C(1)	1.276(3)	N(2)—Pd(1)—O(2)	177.88(8)	O(2)—Pd(1)—N(1)	88.03(8)
Pd(1)—N(1)	2.025(2)	O(2)—C(3)	1.282(3)	N(2)—Pd(1)—O(1)	86.06(8)	O(1)—Pd(1)—N(1)	177.44(8)
Pd(1)—O(2)	2.0119(16)	O(4)—C(3)	1.228(3)	O(2)—Pd(1)—O(1)	92.76(7)	C(1)—O(1)—Pd(1)	121.77(16)
Pd(1)—O(1)	2.0162(18)	O(3)—C(1)	1.224(3)	N(2)—Pd(1)—N(1)	93.07(9)	C(3)—O(2)—Pd(1)	121.40(15)

Table 2

*Torsion angles (τ, deg.) for cis-Pd(NH<sub>3</sub>)<sub>2</sub>(mal)*

Angle	τ	Angle	τ
N(2)—Pd(1)—O(1)—C(1)	-152.2(2)	Pd(1)—O(1)—C(1)—C(2)	5.8(3)
O(2)—Pd(1)—O(1)—C(1)	29.5(2)	O(3)—C(1)—C(2)—C(3)	125.8(3)
N(1)—Pd(1)—O(1)—C(1)	137.5(17)	O(1)—C(1)—C(2)—C(3)	-55.1(3)
N(2)—Pd(1)—O(2)—C(3)	-84(2)	Pd(1)—O(2)—C(3)—O(4)	172.52(18)
O(1)—Pd(1)—O(2)—C(3)	-27.67(19)	Pd(1)—O(2)—C(3)—C(2)	-9.0(3)
N(1)—Pd(1)—O(2)—C(3)	154.76(19)	C(1)—C(2)—C(3)—O(4)	-124.4(2)
Pd(1)—O(1)—C(1)—O(3)	-175.1(2)	C(1)—C(2)—C(3)—O(2)	57.1(3)

Table 3

*Hydrogen bonds for cis-Pd(NH<sub>3</sub>)<sub>2</sub>(mal)*

No.	D—H...A bond	Distances, Å			DHA angle, deg.	Position of the A atom
		D—H	H...A	D...A		
1	N(2)—H(2C)...O(4)	0.89	2.14	3.002(3)	161.8	-x, y+1/2, -z+3/2
2	N(2)—H(2B)...O(4)	0.89	2.49	3.157(3)	132.1	-x+1, y+1/2, -z+3/2
3	N(2)—H(2B)...O(1)	0.89	2.30	3.057(3)	142.5	x+1, y, z
4	N(2)—H(2A)...O(3)	0.89	2.02	2.880(3)	161.5	x+1, -y+3/2, z-1/2
5	N(1)—H(1C)...O(4)	0.89	2.12	2.992(3)	166.3	-x, -y+1, -z+1
6	N(1)—H(1B)...O(3)	0.89	2.28	3.153(3)	165.8	x+1, -y+3/2, z-1/2
7	N(1)—H(1A)...O(2)	0.89	2.63	3.321(3)	134.9	-x+1, -y+1, -z+1
8	N(1)—H(1A)...O(2)	0.89	2.33	3.081(3)	141.7	x+1, y, z

from which it is available free of charge on request at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Selected geometrical parameters are given in Tables 1 and 2. The hydrogen bonds are characterized in Table 3.

**Results and Discussion.** *Cis*-Pd(NH<sub>3</sub>)<sub>2</sub>(mal) has been reported by Nakayama *et al.* [11] who prepared it by the reaction of *cis*-Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> with Ag<sub>2</sub>O to give *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, followed by mixing with malonic acid to produce *cis*-Pd(NH<sub>3</sub>)<sub>2</sub>(mal) with moderate yield (75 %). However, it was characterized only by the elemental analysis. Since Pd(II)—NH<sub>3</sub> bonds are much more kinetically labile than Pt(II)—NH<sub>3</sub> bonds, Barnham *et al* have used [Pd(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> as a starting material to prepare diammine(1,1-cyclobutane-dicarboxylato)palladium(II) with 70 % yield [14]. Malonate is an chelating ligand analogous to 1,1-cyclobutane-dicarboxylate, thus it might participate in a similar reaction with [Pd(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> to produce corresponding *cis*-Pd(NH<sub>3</sub>)<sub>2</sub>(mal). In this context, we studied this reaction and found the yields almost quantitative.

*Cis*-Pd(NH<sub>3</sub>)<sub>2</sub>(mal) crystallized in the form of light yellow block crystals of monoclinic symmetry. The ORTEP drawing of *cis*-Pd(NH<sub>3</sub>)<sub>2</sub>(mal) along with the corresponding atom numbering is shown in Fig. 1, and selected bond distances and angles are listed in Table 1. The Pd(II) atom has a distorted square coordination comprising two N atoms of two ammonia molecules and two O atoms of bidentate malonate ligand with the metal at 0.037 Å out of the mean plane defined by the four donor atoms. As shown in Table 1, the average Pd—N distance is 2.018(7) Å and Pd—O distance is

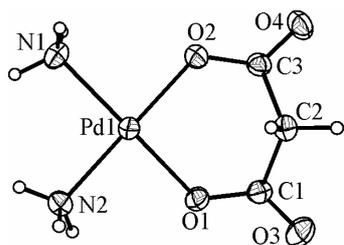


Fig. 1 (left). ORTEP drawing of *cis*-Pd(NH<sub>3</sub>)<sub>2</sub>(mal), displacement ellipsoids at the 50 % probability level

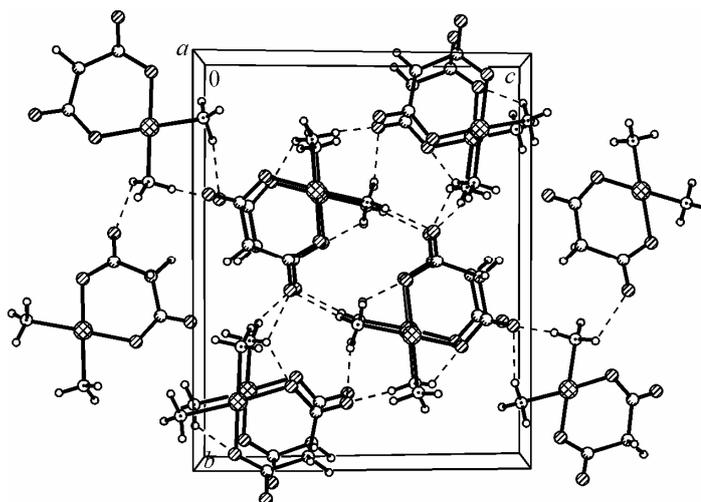


Fig. 2 (right). Weak pairing of *cis*-Pd(NH<sub>3</sub>)<sub>2</sub>(mal) Molecules within the Unit Cell

2.014(2) Å, while the N—Pd—N and O—Pd—O angles are 93.07° and 92.76°, respectively, all of these agree well with the data for related palladium complexes described in the literatures [ 15, 16 ]. When these parameters are compared to the platinum counterpart *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>(mal), the Pd—N and Pd—O distances are slightly shorter than the corresponding Pt—N (av. 2.036(9) Å) and Pt—O (av. 2.022(6) Å) distances, but the N—Pd—N and O—Pd—O angles are almost identical with the N—Pt—N (93.5(3)) and O—Pt—O (92.8(2)) angles [ 9 ]. The six-membered chelate ring formed with the Pd atom adopts the boat conformation as in the structures of other Pd(II) and Pt(II) complexes with malonate [ 9, 15, 17 ].

The crystal packing is stabilized by N—H···O hydrogen bonds (Fig. 2 and Table 3). All three hydrogen atoms of both NH<sub>3</sub> ligands are involved in moderate to strong hydrogen bonding interactions with free or coordinated carboxylate oxygens belonging to adjacent columns, arranging the molecules stacked in such a way that the planes of coordination squares are parallel, the Pd···Pd distance between the nearest neighbors in the stack being equal to 4.039 Å. The molecules within the stacks are connected by additional N—H···O interactions.

**Acknowledgement.** This work was financially supported by Yunnan Provincial Science Foundation of China (No: 2008CC020, 2009CD133) and Provincial Technology Development Program (No: 2008IA008, 2008CF002).

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