

## A Facile Synthesis and Thermal Stability of *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)]

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A simple and facile method for synthesis of *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] has been developed and the thermal decomposition behaviour investigated with TG-DTA under air and nitrogen atmosphere. The complex was prepared by the direct reaction of palladium chloride with ammonium oxalate at mild temperature and the yield was up to 76 %. *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] undergoes the thermal decomposition, respectively, at 180 °C in air and 172 °C in N<sub>2</sub>, leading to the formation of Pd powder and CO<sub>2</sub> and NH<sub>3</sub> as the gas products.

**Key Words:** Diammineoxalatopalladium, Synthesis, Characterization, Thermal decomposition behaviour.

### INTRODUCTION

*cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] is a key intermediate for [Pd(NH<sub>3</sub>)<sub>4</sub>]C<sub>2</sub>O<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>[Pd(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>] which are relatively new Pd complexes and have recently been used as the precursors for palladium-based supported catalysts<sup>1</sup>, for they are soluble in water and do not contain chloride. Chloride was found to have negative effects on some heterogeneous catalysis<sup>2,3</sup>. *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] can be easily converted to [Pd(NH<sub>3</sub>)<sub>4</sub>]C<sub>2</sub>O<sub>4</sub> by dissolving in ammonia and to (NH<sub>4</sub>)<sub>2</sub>[Pd(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>] by reacting with oxalic acid. The synthesis of [Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] was first reported in 1991<sup>4</sup> in which *trans*-[Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] was used as the starting material. The synthetic route involved the quantitative reaction of *trans*-[Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and silver nitrate, which is not acceptable with respect to industrial manufacturing. In this paper, we reported a facile and simple synthetic method of *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] (Fig. 1) along with its chemical characterization and thermal decomposition properties.

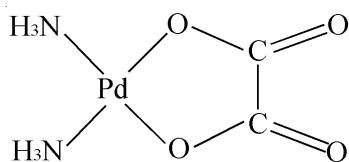


Fig. 1. Structure of *cis*-Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)

### EXPERIMENTAL

The reagents and solvents used were of commercially available reagent quality. Palladium content was determined

according to the reductive-gravimetric method. FI-IR spectra were recorded in the 4000-400 cm<sup>-1</sup> regions on a Perkin Elmer 880 spectrometer with KBr pellets. Thermogravimetric and differential thermal analysis were carried out with a NETZSCH STA 409 PG/PC Jupiter thermo-analysis equipment in air and nitrogen atmosphere (flux rate: 40 cm<sup>3</sup> min<sup>-1</sup>, heating rate: 10 K/min, temperature interval: 25-400 °C, sample mass: 24-25 mg).

### Synthesis

**Synthesis of *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)]:** The powder of PdCl<sub>2</sub> (2.00 g, 11.28 mmol) was slowly added to a solution of (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O (4.80 g, 33.80 mmol) in 120 mL of water at 60-70 °C. After stirring for 10 min, the pH of the mixture was adjusted to 7 by adding NaOH solution drop by drop and the precipitated immediately. The mixture was cooled to room temperature and the yellow product was collected by filtration, washed with cold water and then dried in a vacuum oven at 60 °C. The yield was about 76 %. Found (calculated) for *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)]: Pd 45.98 % (46.56 %). IR (KBr, cm<sup>-1</sup>): 3281, 3187, ν(NH<sub>3</sub>), 1695-1629 ν<sub>as</sub>(COO<sup>-</sup>), 1403-1314 ν<sub>s</sub>(COO<sup>-</sup>), 1248 δ(NHN), 824 ρ(NH<sub>3</sub>) + δ(COO<sup>-</sup>), 783 δ(COO<sup>-</sup>), 558 ν(Pd-N), 477 ν(Pd-O).

**Synthesis of [Pd(NH<sub>3</sub>)<sub>4</sub>]C<sub>2</sub>O<sub>4</sub>:** *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] (1.00 g) was dissolved in concentrated ammonia solution (60 mL) at 70-80 °C, forming a pale yellow solution. After evaporating water and excessive ammonia, a white product crystallized from the solution. The white crystal was collected and washed with icy water and ethanol, dried it in a vacuum oven at 60 °C. The yield was about 76 %. Found (calcd.) for [Pd(NH<sub>3</sub>)<sub>4</sub>]C<sub>2</sub>O<sub>4</sub>: Pd 40.21 % (40.55) %.

**Synthesis of  $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2]$ :** *cis*- $[\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$  (0.70 g) was mixed with water (80 mL) containing  $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (1.17 g) at 60 °C with stirring for *ca.* 1 h and the solution turned red. The solution was condensed to 10 mL to produce a light yellow crystal which was collected, washed with water and then dried in a vacuum oven at 60 °C. The yield was about 77 %. Found (calcd.) for  $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2]$ : Pd 33.14 % (33.42 %).

## RESULTS AND DISCUSSION

*cis*- $[\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$  was synthesized directly from a commercially available reagent  $\text{PdCl}_2$  at 60–70 °C. The yield was up to 76 % and the synthetic conditions were mild and easy to be controlled. Compared with the previous method in which *trans*- $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$  was used as the starting material, the present synthetic route is very effective and cost-saving and can be employed in industrial preparation of *cis*- $[\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$  which can be easily converted to  $[\text{Pd}(\text{NH}_3)_4]\text{C}_2\text{O}_4$  by dissolving in ammonia and to  $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2]$  by reacting with oxalic acid.  $[\text{Pd}(\text{NH}_3)_4]\text{C}_2\text{O}_4$  and  $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2]$  are important water-soluble and chloride-free precursors for industrial production of Pd-based catalysts such as  $\text{Pd}/\text{Al}_2\text{O}_3$ .

*cis*- $[\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$  was structurally characterized by chemical analysis and IR data. The content of palladium is in good agreement with the calculated value. The characteristic bands of  $\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$  in the IR spectrum, as shown in Fig. 2. The binding of  $\text{NH}_3$  and oxalate to palladium(II) atom are confirmed by Pd-N vibration at  $558 \text{ cm}^{-1}$  and Pd-O vibration at  $477 \text{ cm}^{-1}$ . The strong bands at  $3281$  and  $3187 \text{ cm}^{-1}$  belong to the stretching vibration of N-H<sup>5,6</sup>.  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  are responsible for the very strong absorbance bands appearing<sup>7,8</sup>, respectively, at  $1695$ – $1629 \text{ cm}^{-1}$  and at  $1403$ – $1314 \text{ cm}^{-1}$ . Therefore, the chemical analysis and IR data are well consistent with the chemical structure of *cis*- $[\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$ .

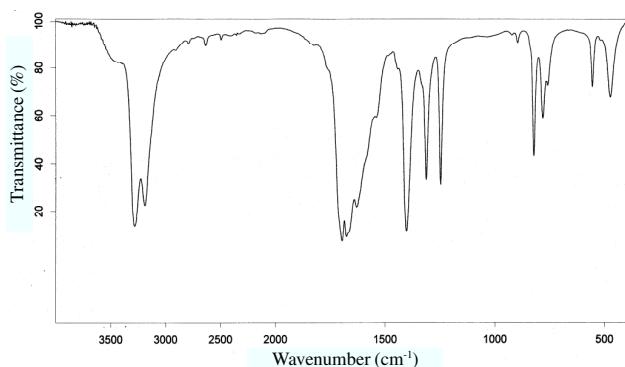


Fig. 2. IR spectrum of *cis*- $[\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$  in KBr tablet

The TG-DTA diagrams of *cis*- $[\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$  under air and nitrogen are shown in Figs. 3 and 4. An apparent weight loss for *cis*- $[\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$  under air occurs at 180 °C, accompanied by an intensive exothermic peak at 202 °C. The weight loss is about 56 % and the solid residue was determined to be Pd powder by XPS analysis. This corresponds to the ligand elimination and oxidation-reduction of *cis*- $[\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$ , forming Pd and  $\text{CO}_2$  and  $\text{NH}_3$  (reaction 1)

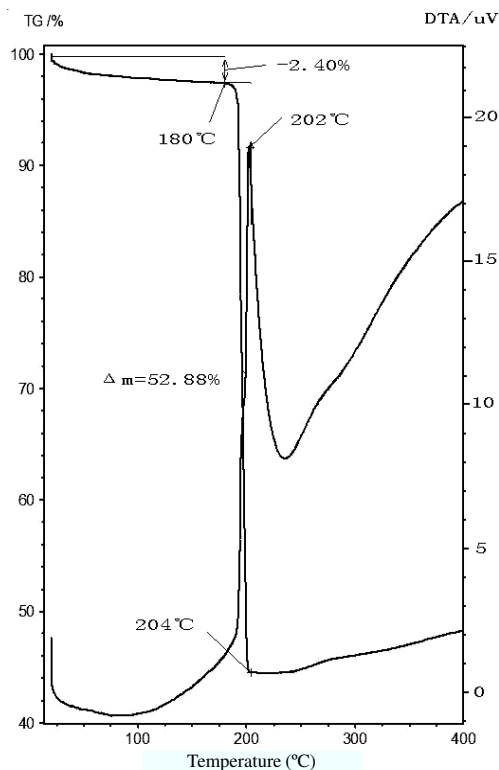


Fig. 3. TG-DTA curves of *cis*- $\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$  in air

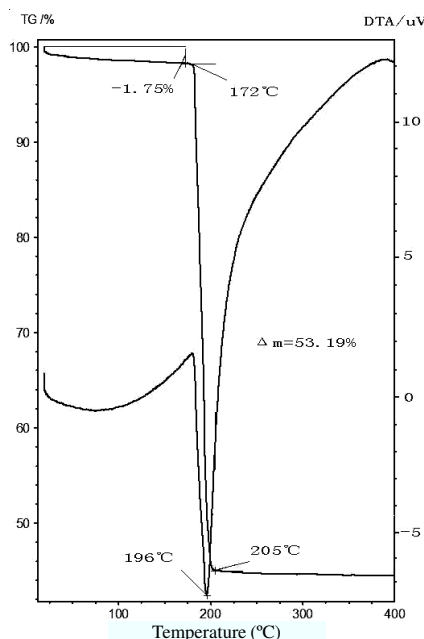
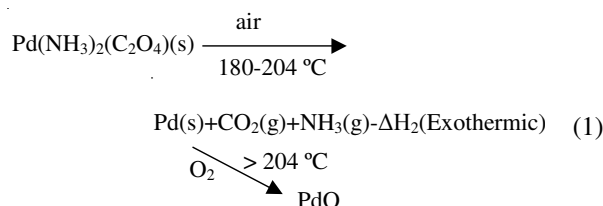
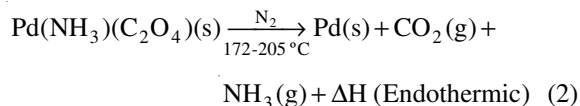


Fig. 4. TG-DTA curves of *cis*- $\text{Pd}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$  in nitrogen atmosphere

As the temperature going up, there is a slow weight gain with exothermic behaviour, which can be explained by the oxidation of Pd to PdO.



Under an atmosphere of nitrogen there is a high weight loss of *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] between 172-196 °C with a sharp endothermic peak. The weight loss is about 56 % and the solid residue was determined to be Pd powder by XPS analysis, similar to the phenomena under the air atmosphere. No significant weight changes are observed as the temperature rises further. All these TG-DTA data indicates that *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] undergoes a intra-molecular oxidation and reduction, giving rise to Pd and CO<sub>2</sub> and NH<sub>3</sub> (reaction 2).



### Conclusion

A simple and facile method for synthesis of *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] has been developed. This synthetic route is very effective and cost-saving and can be employed as an intermediate in industrial production of [Pd(NH<sub>3</sub>)<sub>4</sub>]C<sub>2</sub>O<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>[Pd(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]. Its chemical structure was characterized by chemical analysis and IR. *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] undergoes the thermal decomposition, respectively, at 180 °C in air and

172 °C in N<sub>2</sub>, leading to the formation of Pd powder and CO<sub>2</sub> and NH<sub>3</sub> as the gas products.

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### REFERENCES

1. J.R. Lovie, G.A. Somers and J.J.M. Hendriks, United States Patent Appl. 819968 (1985).
2. J.Y. Sun, Industrial Catalyst Deactivation and Regeneration, Chemical Industry Press, Beijing, p. 84 (2005).
3. H.H. Zhang, M.C. Gong and J.X. Guo, *Chin. J. Catal.*, **25**, 85 (2004).
4. N.Y. Rogin, S.A. Kozlova, N.V. Yakimova, O.I. Borisenko and I.I. Smirnov, *Tsvetn. Met.*, **1**, 35 (1991).
5. Y. Motoyama, H. Kawakami, K. Shimozone, K. Aoki and H. Nishiyama, *Organometallics*, **21**, 3408 (2002).
6. H. Rauter, I. Mutikainen, M. Blomberg, C.J.L. Lock, P. Amoochoa, E. Freisinger, L. Randaccio, E. Zangrando, E. Chiarparin and B. Lippert, *Angew. Chem. Int. Ed. Engl.*, **36**, 1296 (1997).
7. G. Cavinato, A. Vavasori, L. Toniolo and A. Dolmella, *Inorg. Chem. Acta*, **5**, 233 (2004).
8. J. Vicente and A. Arcas, *Coord. Chem. Rev.*, **249**, 1142 (2005).