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# Novel Synthesis and Characterization of $[Pt(NH_3)_4](NO_3)_2$

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A novel synthetic route to $[Pt(NH_3)_4](NO_3)_2$ was developed. The route involved four ligands substitution reactions which were carried out at mild temperatures and under normal pressures. The operations were simple and yield was high. The route of synthesis is acceptable with respect to industrial manufacturing. $[Pt(NH_3)_4](NO_3)_2$ was structurally characterized by elemental analysis and spectroscopic data which suggested that platinum(II) is coordinated to $4NH_3$, forming a bivalent coordinated cation whereas two nitrate ions lie outside the coordinated sphere.

**Key Words: Tetraammineplatinum(II) nitrate, Synthesis, Structural characterization.**

## INTRODUCTION

$[Pt(NH_3)_4](NO_3)_2$, tetraammineplatinum(II) nitrate, is a relatively new Pt(II) complex and has recently been used as the precursor for platinum-based heterogeneous catalysts[1,2] and the intermediate for synthesis of other platinum compounds[3]. It is soluble in water and does not contain chloride which was found to have negative effects on some heterogeneous catalysis[4,5]. The synthesis of $[Pt(NH_3)_4](NO_3)_2$ was first reported in 2005[6] in which $[Pt(NH_3)_4]Cl_2$ was used as the starting material. However, $[Pt(NH_3)_4](NO_3)_2$ is not available in large quantity since it is difficult to prepare $[Pt(NH_3)_4]Cl_2$. In addition, little has been done about its characterization. Herein we report a novel synthetic route for $[Pt(NH_3)_4](NO_3)_2$ and its characterization.

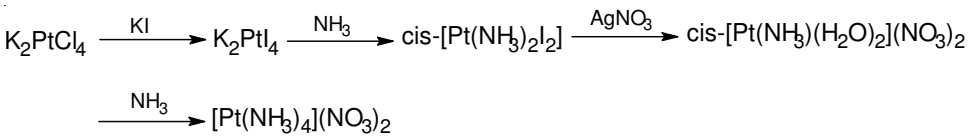
## EXPERIMENTAL

Potassium tetrachloroplatinate(II) ($K_2PtCl_4$) and silver nitrate were purchased from Sino-Platinum Corporation. All other reagents are commercially available and were used without any further purification. Platinum content was determined according to the method in USP22. Mass spectrometry studies were carried out on a ATI-QSTAR Spectrometry in the $ESI^+$-MS. FI-IR spectra were recorded in the 4000-400 $cm^{-1}$ regions on a Perkin-Elmer 880 spectrometer with KBr pellets. $^1H$ NMR was obtained on Bruker AM-400 relative to TMS as an external standard.

$K_2PtCl_4$ (100 g, 240 mmol) was mixed at 45 ºC with KI (240 g, 6 × 240 mmol) in 500 mL of $H_2O$ for 4 h and then 14 % ammonia solution (84 mL, 1.3 × 2 × 240 mmol) was slowly added with vigorously stirring. After standing for 2 h, the resulting

yellow precipitate *cis*-$[Pt(NH_3)_2I_2]$ was collected by filtration, washed with water and ethanol and dried at 65 ºC. The yield was 96 % (112 g). To a suspension of *cis*-$[Pt(NH_3)_2I_2]$ (100 g, 207 mmol) in 500 mL water was added silver nitrate (70.3 g, 414 mmol) and the reaction mixture was stirred at 40 ºC for 36 h. Upon the separation of AgI precipitate the filtrate was condensed at 65 ºC under reduced pressure to 50 mL, followed by addition of 28 % ammonia solution (34 mL, 1.2 × 2 × 207 mmol) again. After complete evaporation of water, a white crystalline product was obtain and dried in a vacuum oven at 60 ºC. Yield: 94 % (76 g). Found (calculated (%) for $[Pt(NH_3)_4](NO_3)_2$): Pt 50.2 (50.4). $ESI^+$-MS: m/e=132 ($[Pt(NH_3)_4]^{2+}/2$, 100 %). IR (KBr, $cm^{-1}$): 3272 s, $\nu(NH_3)$, 1586 m, $\delta_a$(HNH)), 1384 s, $\nu_3(NO_3) + \delta_s$ (HNH), 857 m, $\rho(NH_3)$, 822 m, $\nu_3(NO_3^-)$, 508 m, $\nu$(Pt-N)). $^1$H NMR (DMSO, 500 MHz): 4.07 (12 H, $4NH_3$).

## RESULTS AND DISCUSSION




**Scheme-I**

$[Pt(NH_3)_4](NO_3)_2$ was synthesized according to **Scheme-I** characterized by a four-step route from $K_2PtCl_4$ as the starting material. $K_2PtCl_4$ was converted *in situ* to tetraiodoplatinate(II) by treatment with KI. Addition of ammonia gave rise to the formation of *cis*-diamminediiodoplatinum(II) which was converted to diaquo-diammineplatinum(II) complexes by the quantitative reaction with silver nitrate. Substitution of water molecules with ammine offered the final product $[Pt(NH_3)_4](NO_3)_2$. The yield was up to 90 % and synthetic conditions were mild and easy to be controlled. The reactions involved in the synthetic route are:

$$K_2PtCl_4 + 4KI \rightarrow K_2PtI_4 + 4KCl$$

$$K_2PtI_4 + 2NH_3 \rightarrow cis\text{-}[Pt(NH_3)_2I_2]\downarrow + 2KI$$

$$cis\text{-}[Pt(NH_3)_2I_2] + 2AgNO_3 \rightarrow cis\text{-}[Pt(NH_3)_2(H_2O)_2]\,(NO_3)_2 + 2AgI\downarrow$$

$$cis\text{-}[Pt(NH_3)_2(H_2O)_2](NO_3)_2 + 2NH_3 \rightarrow [Pt(NH_3)_4](NO_3)_2$$

$[Pt(NH_3)_4](NO_3)_2$ was structurally characterized by chemical analysis and spectroscopic data. The content of platinum was in good agreement with the calculated value. It can be seen from Fig. 1 that there were three peak groups developed at m/e = 132, 228 and 244 which corresponded to the molecular ion $[Pt(NH_3)_4]^{2+}/2$ (100 % of relative intensity), $([Pt(NH_3)_4]\text{-}NH_3)$ + and $([Pt(NH_3)_4]\text{-}2NH_3)^+$, respectively. The mass spectra also exhibited typical three protonated molecular ion peaks because of the isotopes $^{194}$Pt(33 %), $^{195}$Pt(34 %) and $^{196}$Pt(25 %). Fig. 2 is the $^1$H NMR spectrum of $[Pt(NH_3)_4](NO_3)_2$. The 12 protons of $4NH_3$ resonated at 4.07 ppm as a singlet in DMSO and the solvent DMSO was responsible for the other two resonances

at 3.36 and 2.49 ppm. The characteristic bands of the complex developed in the IR spectrum, as shown in Fig. 3. The binding of $NH_3$ to platinum(II) atom was confirmed by Pt-N vibration at 508 $cm^{-1}$. A strong band at 3272 $cm^{-1}$ belonged to the stretching vibration of N-H and another intensive band appearing at 1384 $cm^{-1}$

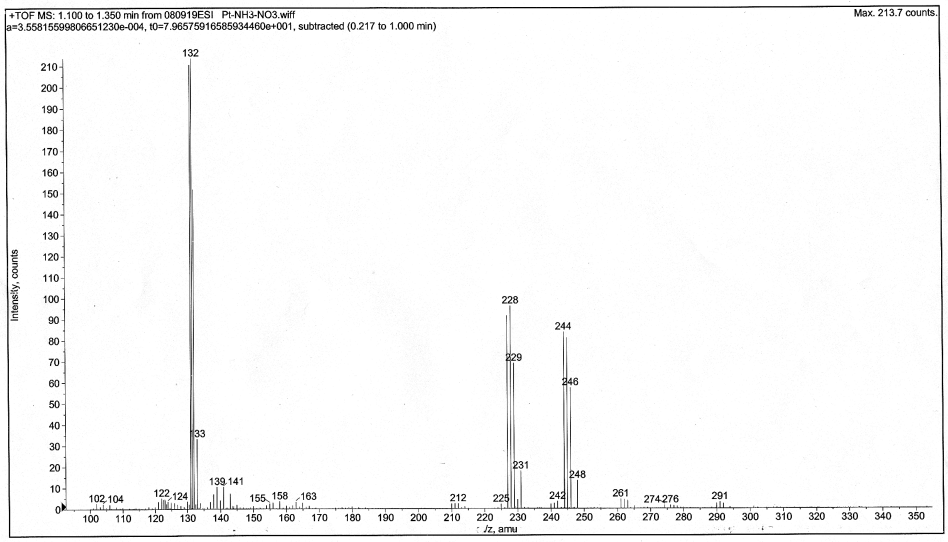



Fig. 1. $ESI^+$-MS spectrum of $[Pt(NH_3)_4](NO_3)_2$ in $H_2O$

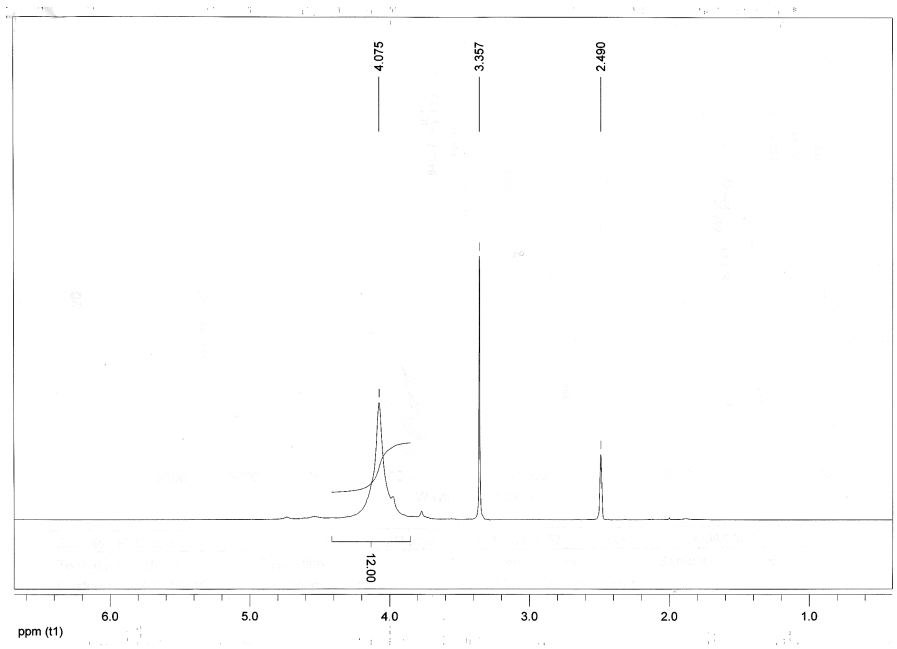



Fig. 2. $^1H$ NMR spectrum of $[Pt(NH_3)_4](NO_3)_2$ in DMSO

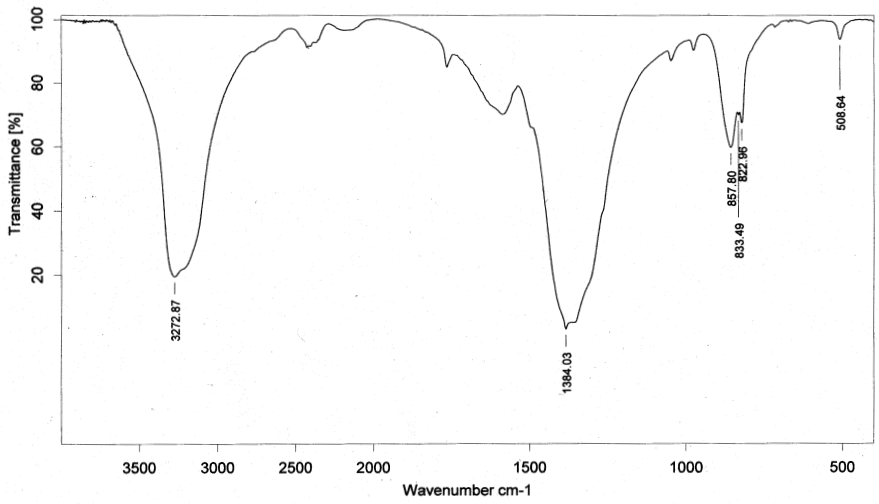



Fig. 3. IR spectrum of $[Pt(NH_3)_4](NO_3)_2$ in KBr tablet

could be assigned to the combination of $\delta_a(HNH)$ and $\nu_3(NO_3)$, $\rho(NH_3)$ and $\nu_3(NO_3^-)$ contributed to the bands near 833 $cm^{-1}$. Therefore, the chemical analysis and spectroscopic data were well consistent with the chemical structure of $[Pt(NH_3)_4](NO_3)_2$. In the molecule of the complex, platinum(II) is coordinated to $4NH_3$, forming a bivalent coordinated cation and two nitrate ions lie outside the coordinated sphere.

## Conclusion

A novel synthetic route to $[Pt(NH_3)_4](NO_3)_2$ was introduced. This synthetic route is very effective and cost-saving and can be employed in industrial production of $[Pt(NH_3)_4](NO_3)_2$. Its chemical structure was characterized by chemical analysis, MS, IR and NMR. In the molecule of the complex, platinum(II) is coordinated to $4NH_3$, forming a bivalent coordinated cation whereas two nitrate ions lie outside the coordinated sphere.

## ACKNOWLEDGEMENT

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