

The Improved Procedure of Hydrazine Dihydro Chloride Method to Prepare Pt (II) Chloride

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Abstract

Potassium tetrachloro platinum (II) complex was synthesized by the redox reaction between potassium hexachloro platinum (IV) and hydrazine dihydrochloride as a reducing agent. During the preparation processes certain circumstances lead to the improvement of the percentage yield and its purity and prevent its conversion to platinum metal. The prepared materials (hydrazine dihydrochloride, potassium hexachloro platinum (IV) and potassium tetrachloro platinum (II) was identified by spectral techniques (UV-Visib., FTIR and XRD) and the physical constants and properties of the products. The final product (potassium tetrachloro platinum (II) was a red needle crystals that confirm its good purity. The percentage yield was 98%.

Keywords: Hydrazine dihydrochloride, potassium hexachloro platinum (IV) salt, potassium tetrachloro platinum (II) salt, XRD analysis.

الخلاصة

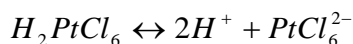
ملح البلاتين الثنائي للبوتاسيوم حضر بواسطة تفاعل أكسدة واختزال بين ملح البلاتين الرباعي للبوتاسيوم وكلوريد الهيدرازين كعامل مختزل. استخدمت في عملية التحضير ظروف معينة أدت إلى تحسين النسبة المئوية للمنتج ونقاوته والحيلولة دون تحول البلاتين إلى الفلز الحر الأسود. شخّصت المواد الحاضرة (كلوريد الهيدرازين وملح البلاتين الرباعي وملح البلاتين الثنائي) باستخدام التقنيات الطيفية (UV-Visib., FTIR, XRD) بالإضافة إلى الثوابت والخواص الفيزيائية للنواتج. تم الحصول على البلاتين الثنائي بشكل ابر حمراء بلورية كبيرة الحجم مما يدل على نقاوتها العالية ونسبة منتج 98%.

الكلمات المفتاحية: الهيدرازين ثنائي هايدروكلورايد، بوتاسيوم سداسي كلورو بلاتين الملحي (IV)، بوتاسيوم رباعي كلوروبلاتين، تحليل اشعة X.

Introduction

Platinum (II) salts have wide importance in medical drugs field, since the discovery of its activity as anticancer reagents in 1960 until now, its regarded as the primary material for the preparation of all the different types of a platinum basic anticancer drugs, which is one of many types of chemotherapy drugs (Rosenberg, 1971; Guo, 2000; Rebbecca, 2006). The first beginnings to reduced platinum (IV) to platinum (II) used many inorganic reagents as shown below. (Claur, 1858), after him (Nilson, 1877), used sulfur dioxide solution as a reducing agent to convert platinic (IV) acid to platinic (II) acid and then convert it to its salts as chlorides or carbonates. (Vezes, 1898) after him (Klason, 1904) used potassium oxalate as a reducing agent. (Lea, 1894) used potassium hypophosphate as a reagent and potassium hydrogen sulfite as a reagent for another procedure. (Bottger, 1864) used hydrogen sulfite as a reducing agent for this reaction. (Thomsen, 1877) used copper (I) chloride for this reaction as a reducing agent. (Keller, *et al* 1964) used the hydrazine as a reducing agent. (Kauffman *et al*, 1963) used hydrazine hydrochloride for this purpose. (Milne, 2005) used hydrazine sulfate as a reducing agent for purpose. (Chatt *et al.*, 1981) used hydroxyl amine hydrochloric acid as a reducing. Among these different reagents, (Rhoda, *et al.*, 1981) used hydrazine dihydrochloride as a reagent with good yield by applied many improvements to reach to this results. In

these research, an improved method was innovated to reduce platinum (IV) to platinum (II), by using the hydrazine dihydrochloride as a reducing agent, by applying many attentions and parameters such as, the amount reducing agent and the situation of reactions to achieve good purity and high product (John *et al.*, 1956). Hexaplatinic acid (H_2PtCl_6) is a strong dibasic acid and ionizes as:



Thus, this acid gives the stable salts of the type $M_2^+ [PtCl_6]^-$, where $M^+ = Li^+, K^+$ etc., which are called hexachloro platinates of M^+ . Examples of such salts are K_2PtCl_6 (Satya, 2000).

Experimental

Materials

All the used reagents were of analog regarded. Water was doubly distilled and strong in glass Stoppard flasks. Potassium hexachloro platinate (IV) complex was prepared from the standard platinic (IV) acid from sigma Aldrich company 99% purity. Hydrazine reagent is from B. D. H Company 98%.

Apparatuses:

- 1-The electronic spectra were recorded for the aqueous solutions of the salts and for the ethanolic solution of the hydrazine and hydrazine dihydrochloride by using (UV-6100PC Double beam spectrophotometer, EMCLAB, Germany).
- 2-FTIR analysis was carried out by (Fourier Transform Infrared spectrophotometer Shimadzu, Japan, measurements were conducted in the wave numbers ranged from 400-4000 cm^{-1}).
- 3-PH measurements were carried out by (Inolab WTW PH meter).
- 4-X-Ray Powder Diffraction (XRD) patterns were investigated by using XRD 6000 X-Ray Diffractometer apparatus' for the platinum salts under investigation.
- 5-All these analysis were done at chem. Dep. Labs of Babylon University except the XRD, which done at material college in University of Babylon.

Preparations:

Step1:

Preparation of hydrazine dihydrochloride:

The procedure is similar to that reported by (Schmidt, 1984) and that reported by (Bernard, *et al*, 1961). Concentrated hydrochloric acid (14.6ml) added drop wise to cold hydrazine mono hydrate (6.5ml) under constant stirring with cooling to ($-2^\circ C$). The solution was heated for 5 minute at $50^\circ C$ to concentration it, then, the solution brought back to room temperature and conc. HCl (16.3ml) was again added under stirring in cold bath water, soon the white precipitate formed and filtered and washed with absolute methanol. Its M.P. was $200^\circ C$, percentage yield was 75%.

Step2:

Preparation of Potassium hexachloro platinate (IV) complex:

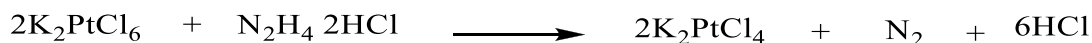
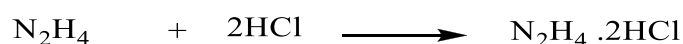
Saturated solution of KCl (1.5g dissolved in 20ml D.W.) added drop wise to a solution of platonic (IV) acid (1g dissolved in 10ml D.W.), soon a yellow precipitate of potassium, hexachloro platinum (IV) complex was formed. 10ml of absolute ethanol was added to it and the solution was colder in ice bath water, filtered, washed with ethanol, dried in room temperature and weighed. The percentage yield was 98%.

Step3:

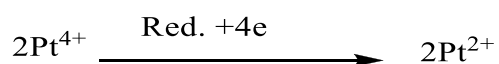
Preparation of potassium tetrachloro platinate(II) complex:

Above saturation solution of potassium hexachloride platinate(IV) complex (3g in 20ml D.W.) was put in bath water at 40-50 °C under stirring. 0.01g of hydrazine dihydrochloride was added to each half hour until a suspension red solution was formed. The solution was cooled. The filterer was left under room temperature for 3-4 days. A needle red crystals of potassium tetrachloro platinum (II) complex was grown. The reaction takes about two hours. This procedure was repeated for the residual precipitate on the filter paper.

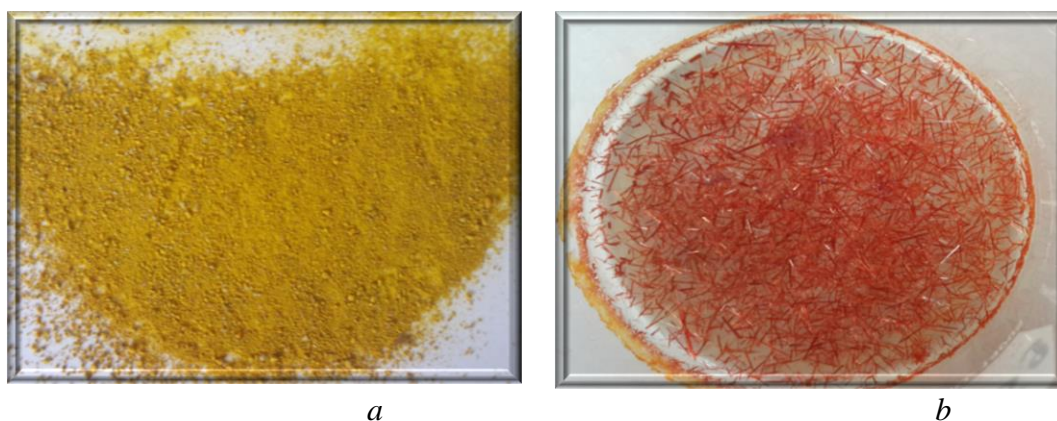
Schem1:- show all these reaction. The yield percentage was 98%. Schem2:- show the images of the salts.



Redox Reaction:



Schem1:- steps for the preparation of K_2PtCl_4



Schem2:- show the images of the salts a: K_2PtCl_6 salt, b: K_2PtCl_4 salt.

Results and Discussion

Many physical properties and techniques were used to identify the prepared materials as shown below:

1-The physical and appearance properties

- *Hydrazine dihydrochloride was a white powder which obtained from a liquid hydrazine, its melting point is $201^\circ C$.
- *Potassium hexachloro platinum (IV) complex, obtained from the orange platinic acid powder, was a yellow powder which was decomposed by heating to platinum metal.
- *Potassium tetrachloro platinum (II) complex, was a red needle crystals, which decomposed to platinum metal by heating.

2-UV-Visb. spectra; by which, the electronic absorption spectra for aqueous solutions of platinum salts were recorded, as shown in Figures(1) and(2) including a bands at 268nm and 220nm of the Pt (IV)and Pt (II) salts respectively, hence then is a 30nm as a blue shift confirming a new compound obtained. The electronic absorption spectra for ethanolic solutions of hydrazine and hydrazine dihydrochloride were recorded as shown in Figures(3) and(4) including two bands at 228nm and 222nm respectively, hence there is a 30nm red shift confirming anew compound was obtained.

3-FTIR spectra; were recorded for the liquid hydrazine and for the solid hydrazine dihydrochloride with range $(400-4000cm^{-2})$ with KBr disc. The important peaks of the FTIR spectra are summarized in Table(1,2) (Daniela, 2006; Manimekalai, *et al*, 2012) N-H stretching and bending bends shifted to low energy due to the formation of $-NH_3^+$ ion in hydrazine dihydrochloride, where in N-N was shifted to high energy. The disappear of N-H wagging band in hydrazine was confirming the formation of hydrazine dihydrochloride. Figures(5)and(6) show the FTIR spectra of these reagents, respectively.

4-XRD Patterns; were recorded for the platinum (IV) salt and platinum (II) salt,

including a main peak at $2\theta = 15.72^\circ$, and a main peak at $2\theta = 12.7^\circ$ respectively, by using Cu target, voltage 40Kv and current 30mA. By the comparison of these patterns with standard ones of these salt confirming the formation of these salts with high purity. Figures(7)and(8) show the patterns of XRD for these salts, respectively.

Table 1: Important FTIR spectral frequencies for the hydrazine and hydrazine dihydrochloride.

Assignment(cm^{-1})	Hydrazine	Hydrazine dihydrochloride
(N-H)stretching	3346s	3003m
(N-H)bending	3194s	1481s
(N-N)stretching	1612s	1067s
(N-H)wagging	1062s	

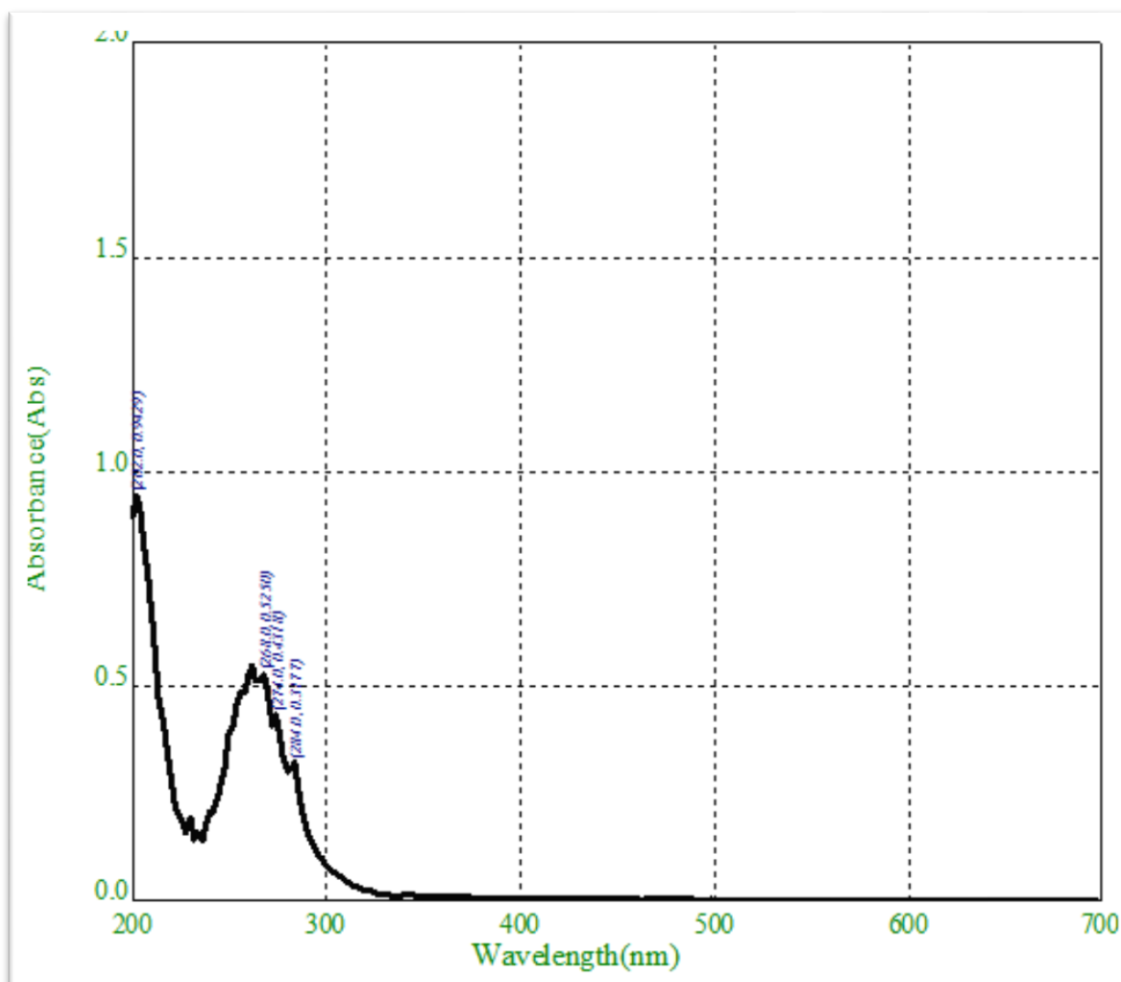


Figure1 :UV-Visb. spectra for K_2PtCl_6 .

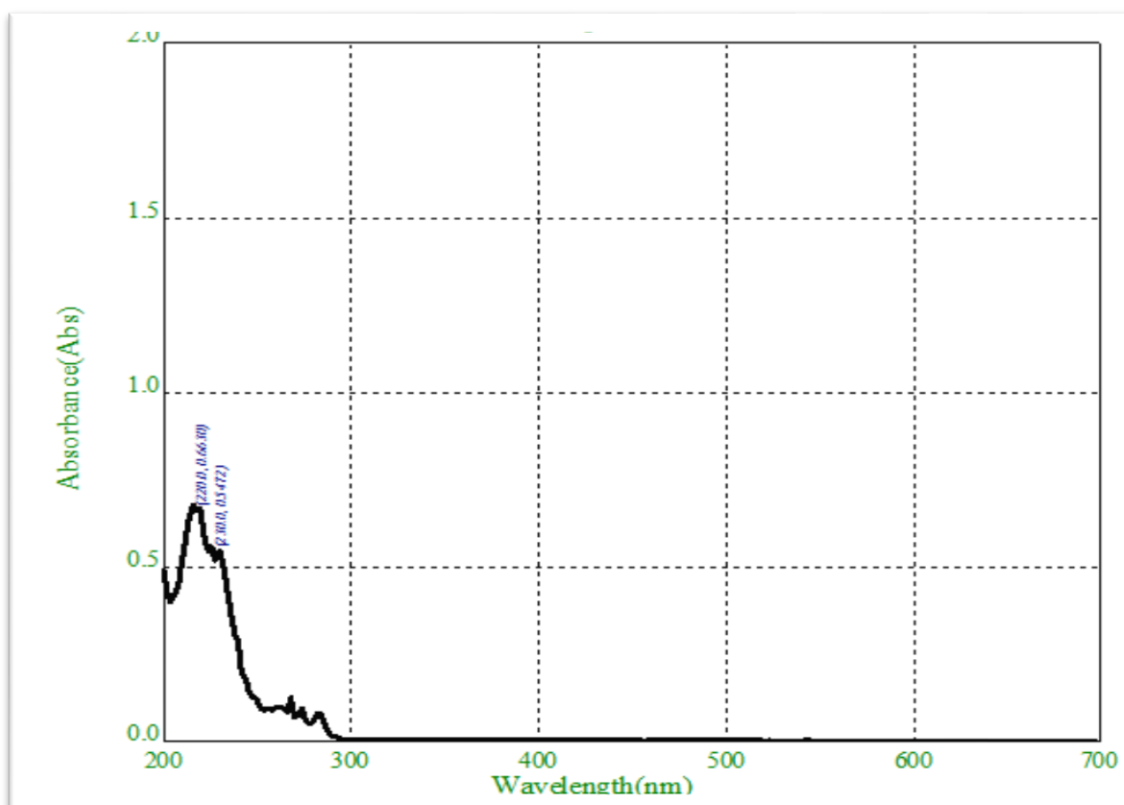


Figure 2:UV.Visb. Spectra for K_2PtCl_4 .

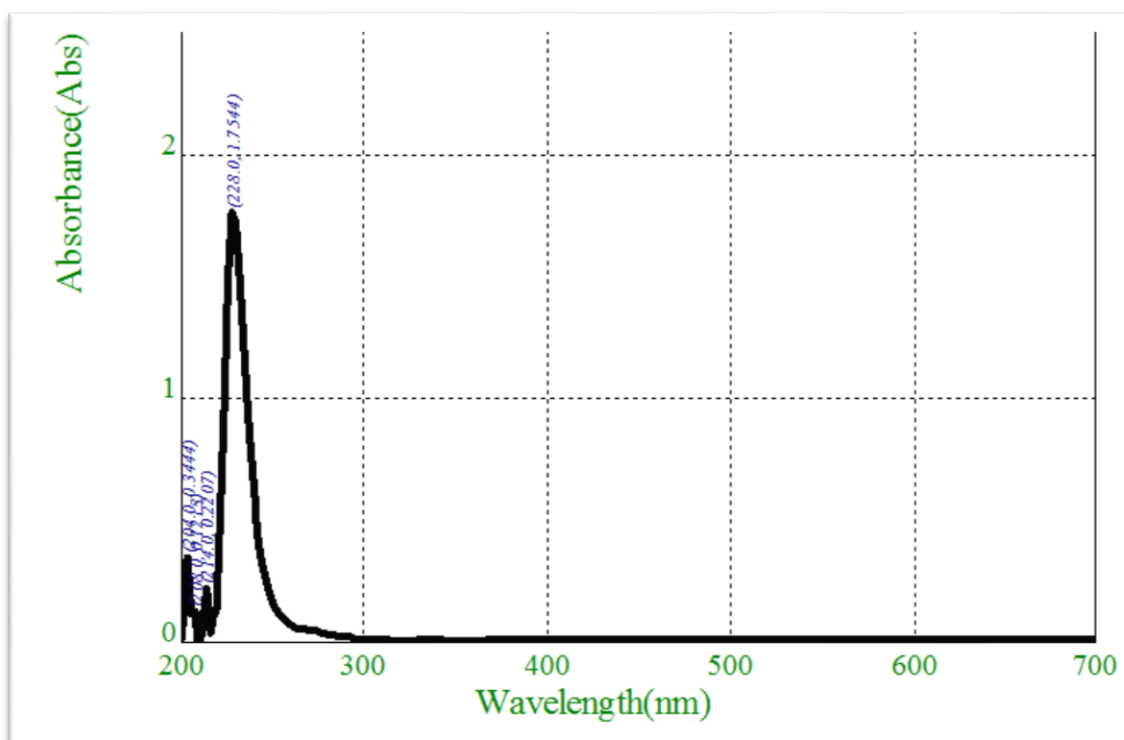


Figure 3: UV.Visb. Spectra for N_2H_4 .

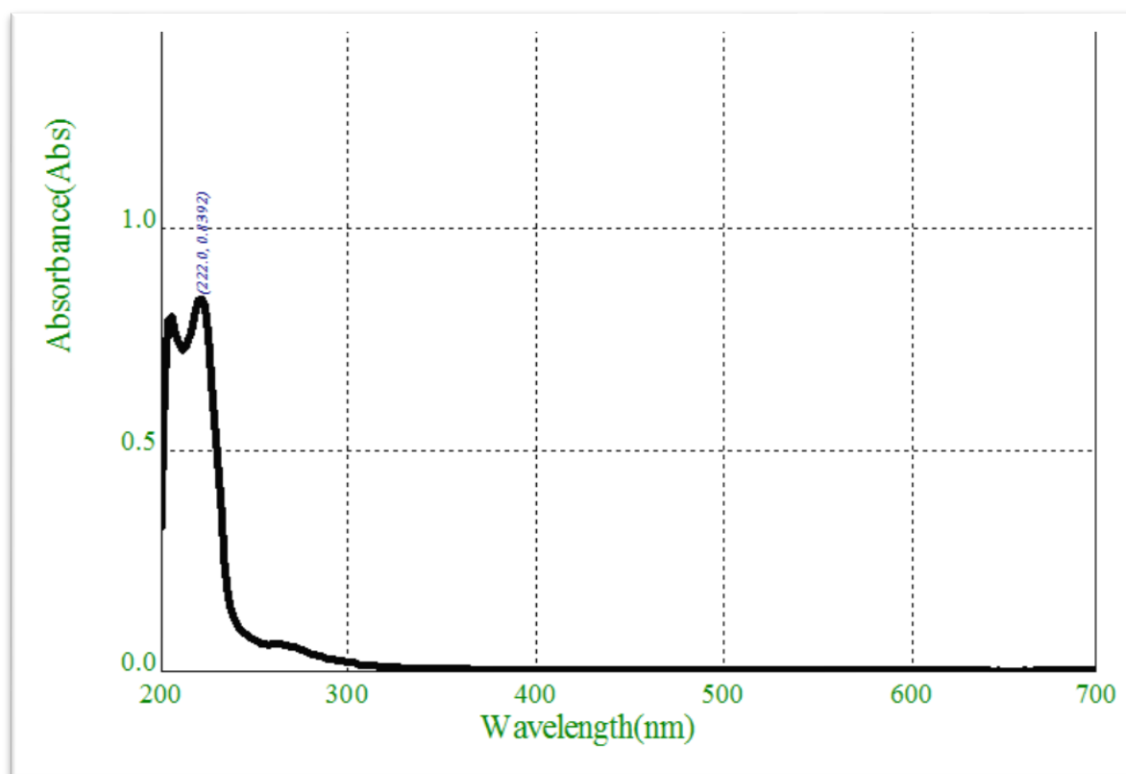


Figure 4: UV.Visb. Spectra for $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$.

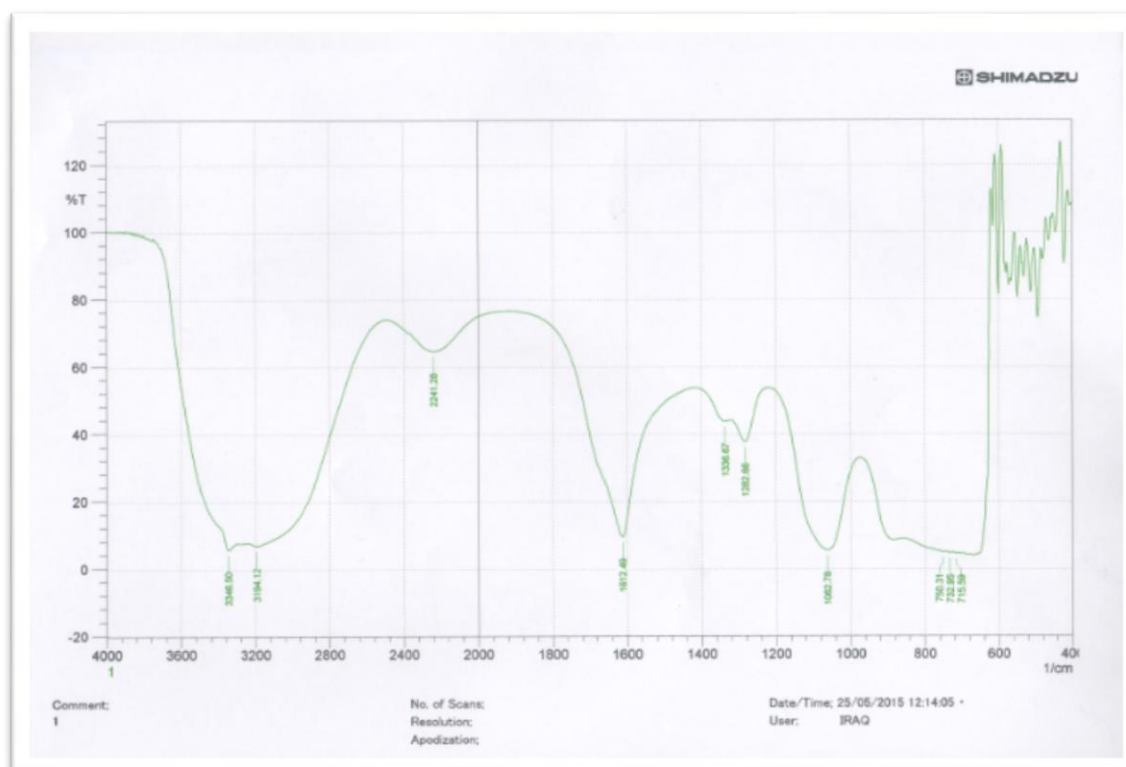


Figure 5: FTIR Spectra for N_2H_4 .

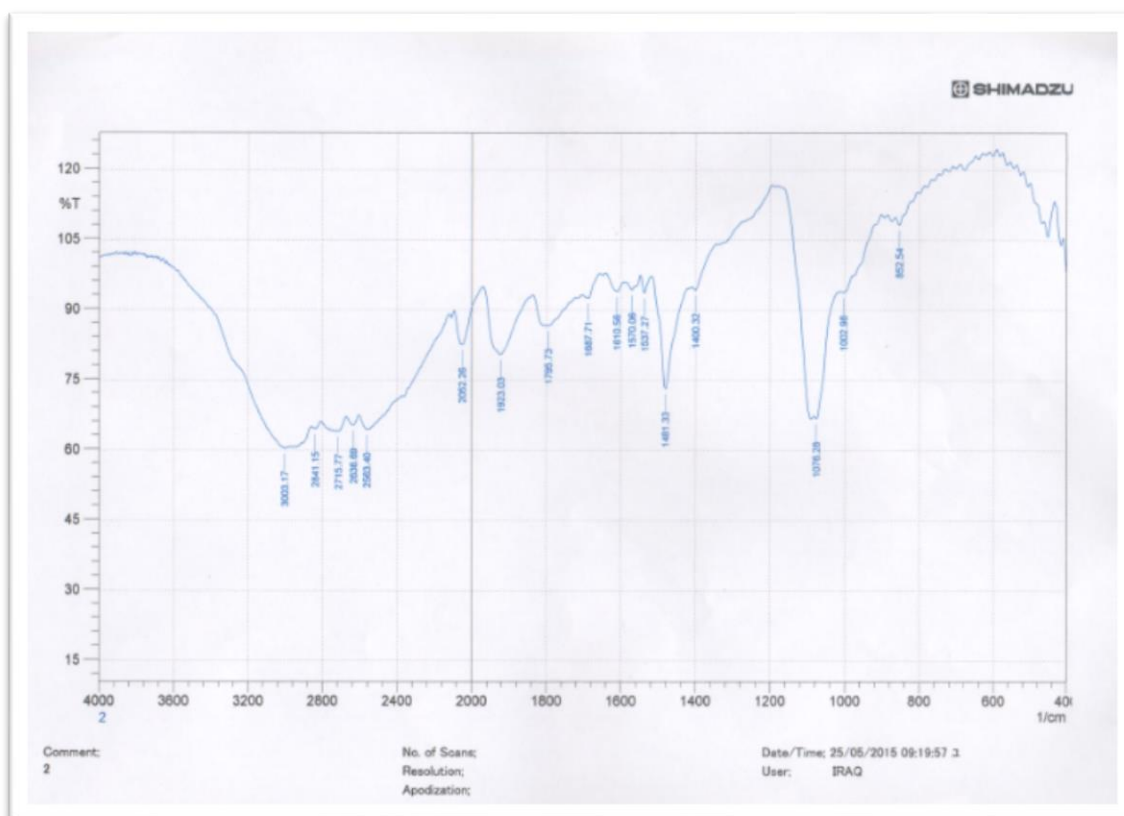


Figure 6: FTIR Spectra for $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$.

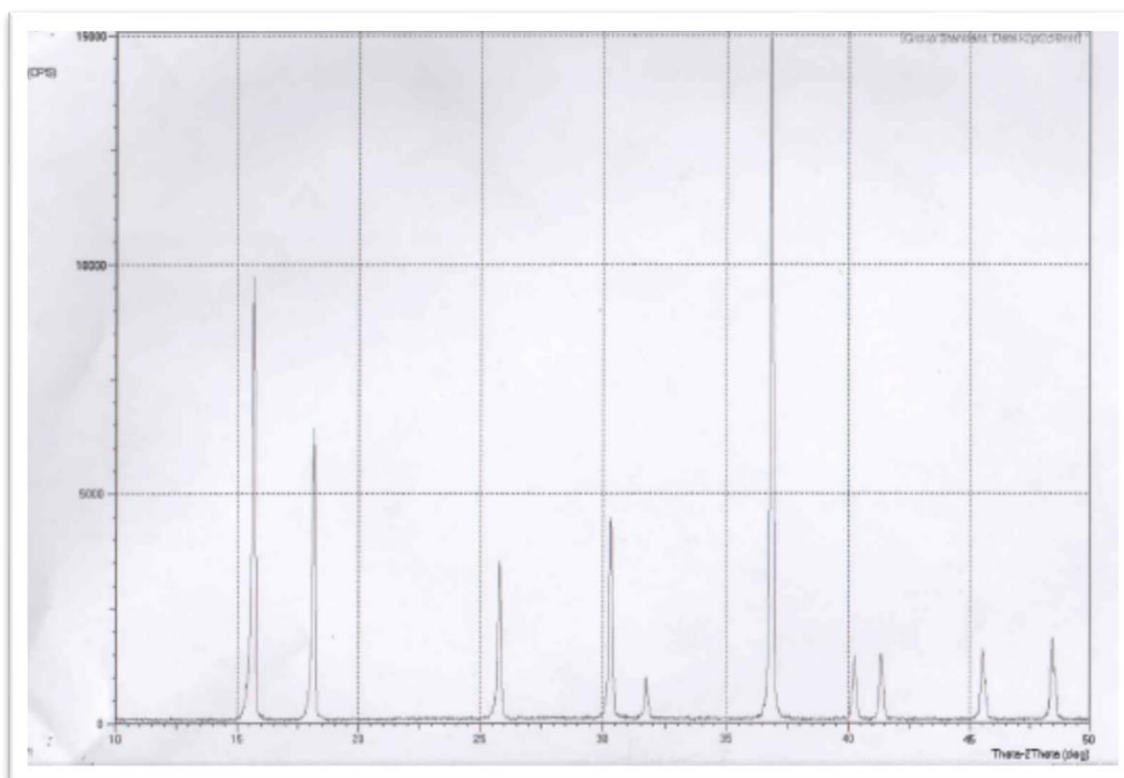


Figure 7: XRD Pattern for K_2PtCl_6 .

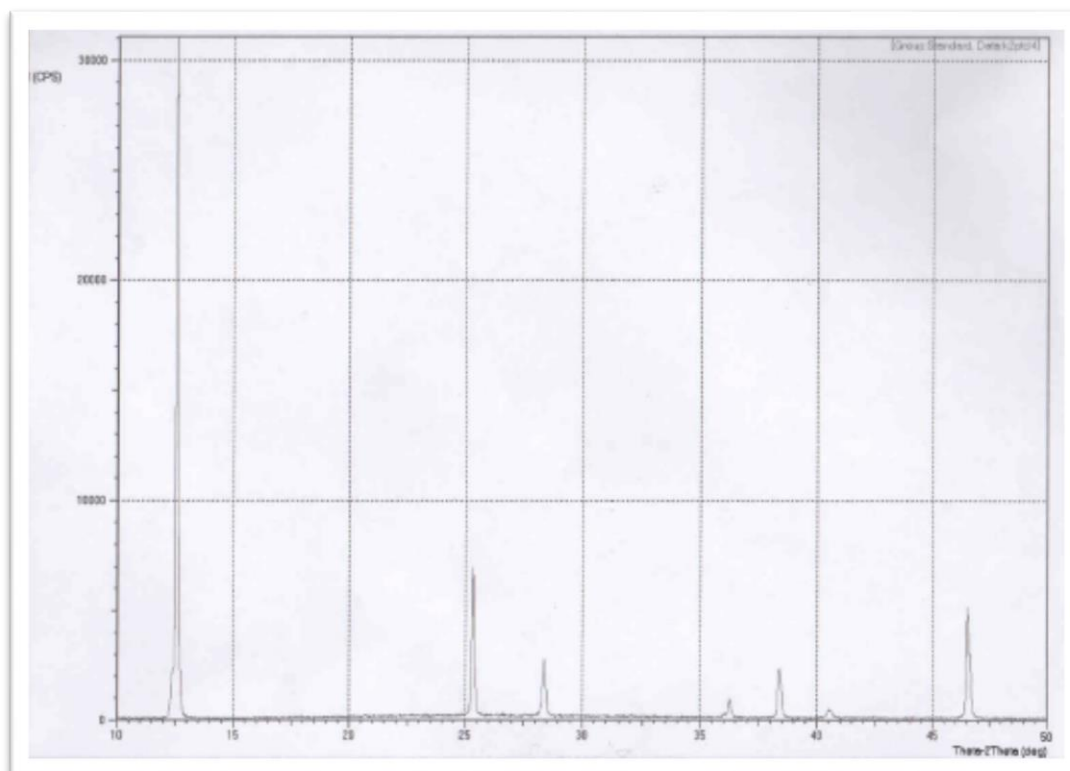


Figure 8: XRD Pattern for K_2PtCl_4 .

Conclusion

The main problem in converting process of platinum(IV) to platinum(II) is that the platinum(II) is very active towards the red ox reactions, therefore, at race excess of the reducing, agent cause, to reduction Pt (II) to platinum metal and may be Pt (IV) converted to platinum metal directly above 50C in the existence of reducing agent.

The advantages of the method used in this paper are:

- 1-High yield of the product
- 2-Pure crystal of Pt (II) salt.
- 3-Easy procedure, so it accomplished with freedom without conversion of Pt (IV) to platinum metal.

The circumstances were used to improve the yield in this paper, are:-

- 1-Using over- saturated solution of potassium hexachloro platinum (IV) to ensur the preventing of reduction process of Pt (II) to platinum metal.
- 2-Keeping the temperature at (40-50) °C and avoiding a height of more than that
- 3-Controlling on the amount of reducing agent so that very little is added to (0.01g) (every half hour).
- 4-Avoiding adding any other amount of reducing agent when the yellow suspension solution turned to red.
- 5-The presence of increased platinum(IV) sponsor that will prevent the reduction of platinum(II) to metal because the 4+ charge on platinum(IV) is that attract the electrons generated from the reducing agent and not a 2+ charge on platinum(II) do that.

- 6-In case of expiration of platinum (IV) from the solution, the process of converting of platinum (II) to platinum metal will begin.
- 7-All the above steps- hold them to the remaining quantity of platinum (IV) after separation of the red solution by filtration. This step sponsor increase the percentage of product
- 8-The use of drying at room temperature sponsor to prevent the reduction in case of using thermal drying
- 9-The use of absolute ethanol for washing the products increase the purity of them

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