# Syn the sis of New Re agent 2-Acetylthiophenethiocynate and its Use in Extraction of Pt(IV) Spectro photometrically

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2-Acetyl thiophenethiocynate (ATT) was syn the sized and its char ac ter iza tion study was car ried out using el e men tal anal y sis, IR and NMR tech niques. The new re agent was pro posed as an extractant for the de vel opment of the ex trac tive spec tro pho to met ric method for de ter mi na tion of Pt(IV) metal. The re agent complexes with the metal to pro duce a yel low col ored com plex which was then ex tracted into ethyl ac e tate at pH 11.2-11.6 hav ing an ab sorp tion max ima at 400 nm. The ther mal study showed that the ex trac tion re actions are exo ther mic in na ture with the re agent, and the stoichiometric ra tio of Pt(IV) to 2-acetyl thiophenethiocynate in the or ganic phase was 1:2. The method per mits sep a ra tion and de ter mi na tion of plat i num from real and binary mix tures. The sep a ra tion of Pt(IV) from bi va lent metal ions has been also stud ied.

# INTRODUCTION

Organosulfur com pounds are clas si fied as soft bases, which pref er en tially re act with soft acid met als, like Pt(IV), Pd(II), Au(III), and Ag(I) ac cord ing to Pearsen's HSAB principle. When dialkalysulfides and the corresponding sulfoxides are employed for no ble met als, ex trac tions showed<sup>1</sup> sul fides to be su pe rior to sulfoxides. On an in dus trial scale (INCO) Pt(IV) was ex tracted by dialkyl sul fides.<sup>2</sup> The di rect ex trac tion of Pt(IV) was found to be very poor with 2-ethyl hexyl phosphonic acid mono-2-ethylhexyl es ter (PC-88A),<sup>3</sup> triphenyl phos phine (TPP),<sup>4</sup> deriv a tives of thiourea,<sup>5,6</sup> and dithizone,<sup>7,8</sup> in CCl<sub>4</sub> from chlo ride me dia, and was pos si ble only after reduction of Pt(IV) to Pt(II) by stan nous chloride.<sup>9</sup> The extraction of platinum(IV) and palladium(II) was studied with amines,<sup>10</sup> diamines,<sup>11</sup> and TOA;<sup>12</sup> while TOA is used on an in dus trial scale, these all suf fer from long equi lib rium time. The novel extractant, 3,3-diethylthietane (DETE)<sup>13</sup> could not give a quan ti ta tive ex trac tion of Pt(IV) from chloride me dia. The derivatives of calix [4] arene<sup>14</sup> are also used as phase trans fer re agents for ex trac tion of Pt(IV) from chlo ride media.

The ex trac tion with TOPO<sup>15</sup> from chlo ride me dia has also been re ported. Sev eral ox imes, semicarbazones and thiosemicarbazones have been re ported which form complexes with met als and are found use ful in com mer cial ap plications.<sup>16</sup> These types of re agents have been used to find out quan ti ta tively the per cent age of com position in binary mixtures and from real sam ples. These re agents ex tract the metal through the sol va tion method. How ever there has been lit tle done on ex plor ing the pos si bil ity of us ing thiocynate de riv a tives as extractants. The thin layer chro mato graphic and electro pho retic study of the chlorothiocynato com plex of plat i num is re ported.<sup>17</sup> The mix ture of thiocynate and rhodamine 6G was used to carry out spec tro pho to met ric de ter mi na tion of plat i num(IV) in mi cro amounts.<sup>18</sup> Ex trac tive spec tro pho to met ric de ter mi na tion of no ble met als has been de scribed ear lier; how ever the method adopted re quire sev eral ex traction stages for quantitve ex trac tion of plat i num(IV). To develop a more ef fec tive method, by ex trac tive spec tro pho to metric de ter mi na tion of plat i num(IV).

In this communication we present syn the sis of a new reagent and method for ex trac tion of Pt(IV) from aque ous media at a partic u lar pH in the presence of various met als using 2-acetyl thiophenethiocynate (ATT) as an extractant in ethyl ac e tate using a UV-spectrophotometer at 400 nm.

# EXPERIMENTAL

#### Equipment

Absorbance and pH mea sure ments were car ried out on a Shimadzu UV vis i ble 2100 spectrophotometer with 1 cm quartz cells and a Con trol Dy namic dig i tal pH me ter with com bined glass elec trode, respectively.

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#### Synthesis of Ligand

The mod i fied syn the sis procedure for preparation of thiocynate is proposed. The reagent 2-acetyl thiophene thiocynate (ATT) was prepared ac cord ing to a mod i fied procedure, which is de scribed in Vogel.<sup>19</sup>

2-Acetyl thiophenethiocynate (ATT) was syn the sised as follows. In the first step the bromination of 2-acetyl thiophene was car ried out tak ing an equimolar con cen tration and sol vent as gla cial ace tic acid and the bro mine was added dropwise for an hour at 4 °C and then stirred for three hours for its complete reaction. The reaction mix ture was de composed on ice and then the prod uct was sep a rated with ethyl ac e tate by a sep a rat ing fun nel and then pro cessed. The ethyl acetate was distilled out under vaccum leaving the brominated com pound which was stirred with potassium thiocynate (ra tio 1:2) tak ing sol vent as DMSO at room tem per ature for 8 hrs. The re ac tion mix ture was de com posed on ice and the yel low solid which sep a rated out was recrystallised and used for fur ther stud ies. The m.p. re corded was 97 °C. The char ac ter iza tion of the prod uct was car ried out with the help of IR which shows stretching of C=O at 1640 and stretch ing of SCN at 2020, NMR in CDCl<sub>3</sub> which shows  $\delta$  4.5 (2H, s, -CH<sub>2</sub>-); δ 7.0-7.33 (1H, t, H<sub>4</sub>); δ 7.66-8.0 (2H, m, H<sub>3</sub> and  $H_5$ ) and el e men tal anal y sis re corded was C, 45.88; H, 5.88; N, 16.33; O, 12.44%. The yield of the prod uct re corded was very low i.e 22.38%.



#### **General Procedure**

Extraction experiments were performed by shaking the ap propriate or ganic and aque ous solution at an O/A phase ratio of 1 for 10 min. The distribution studies were carried out at 25 °C, exceptfor the effect of temperature. The initial concentration of Pt(IV) was main tained at 50  $\mu$ g through out the experiment The ATT extractant formed a complex with platinum(IV), was transferred in to a separating funnel, extracted in ethyl ac e tate (2 × 5 mL) and transferred to a 10 mL volumet ric flask with some amount of so dium sulfate in or der to

ab sorb trace amounts of wa ter. The amount of plat i num metal present in the or ganic phase was deter mined quant it a tively by U.V. spectrophotometry. The distribution coefficient, D, was cal cu lated as the ratio of the Pt(IV) in the or ganic phase to that of the aque ous phase. Trip li cate exper i ments and assays were rou tinely per formed. In gen eral, D had a stan dard deviation of  $\pm$  5%. The uncertainty in terval was higher for the very high (D > 100) or very low (D < 0.01) D values. The deter mination of plat i num(IV) in the or ganic phase was cal culated by tak ing absorbance at 400 nm spec trophotometrically and that in aque ous was determined by a known method.

#### Reagents

The stock so lu tion of plat i num(IV) was pre pared by dis solv ing 0.10 g of hexachloroplatinic acid in 100 mL distilled water. The so lu tion was stan dard ized<sup>20</sup> and a work ing so lu tion of lower con cen tra tion was ob tained by suit able dilution. 2-Acetyl thiophenethiocynate (ATT) dissolved in meth a nol was used as extractant. A 0.1% so lu tion of 2-Acetyl thiophene thiocynate (ATT) was used for spec tro pho to met ric de ter mi na tion of plat i num(IV). All the other chem i cals used were of an alyti cal re agent grade.

#### **RESULTS AND DISCUSSION**

# Extraction as the function of pH

In or der to obtain the optimum extraction conditions for platinum(IV) the extraction was carried out at various pH values (2.0-12.0) (see Fig. 1) us ing 0.1 M hy dro chlo ric acid or 0.1 M so dium hy drox ide so lution. The concentration of platinum(IV) (50  $\mu$ g) was taken in aq. phase and to it 2.0 mL of ATT (0.1%) was added. The pres ence of plat i num(IV) in



Fig. 1. Percentage extraction of complex of Pt(IV) with ATT in ethyl ac e tate at different pH.

aque ous phase at dif fer ent pH was stud ied by the stan dard method and was found that in the pH 11.2-11.6 range the pres ence of plat i num(IV) was least. It was ob served that 0.5 mL of 0.1% ATT dis solved in meth a nol quan ti ta tively extracts plat i num from aque ous so lu tion at pH 11.2-11.6. It is pro posed that the ni tro gen of the thiocynate func tional group and sul phur of thiophene in al ka line me dium helps in ex tracting plat i num(IV) metal ions from an aque ous me dium.

#### Ef fect of equi lib rium time

The in flu ence of shak ing time for the ex trac tion of Pt(IV) was studied for 30 s to 120 s. The quant it a tive ex traction of Pt(IV) was achieved after 60 s with ATT. With fur ther in crease in shak ing time, the per cent age ex traction remained quant it a tive. The sta bil ity of the com plex was studied as a function of time and found that the com plex was sta ble for 72.0 h.

# **Influence of diluents**

The suit abil ity of the dil u ents was in ves ti gated us ing organic solvents such as chloro form, ethyl ac etate, ethyl methyl ketone, methyl isobutylketone, n-butanol, car bon tetrachloride, to luene, and hexane. The extraction of platinum(IV) was quan ti ta tive with ATT when both were dissolved in aque ous solution tak ing ethyl ac etate as dil u ent (see Table 1). Ethyl ac etate was used for fur ther extraction stud ies as it gave better and quicker phase sep a ra tion. The extract ion of Pt-ATT com plex from aque ous me dia into ethyl ac e tate was max i mum (up to 99.0%) than the other or ganic sol vents. So ethyl ac e tate was cho sen as an extract ing sol vent for further stud ies.

#### The influence of temperature

The ex trac tion study of Pt(IV) was per formed at dif fer-



Fig. 2. Effect of tem per a ture on extraction of Pt(IV) with ATT in ethyl ac e tate from aque ous me dia.

Table 1. Distribution Coefficient of Pt:ATT Complex in Various Organic Solvents

| Solvent               | % E  | D     |
|-----------------------|------|-------|
| Chloroform            | 25.0 | 0.333 |
| <i>n</i> -Butanol     | 10.0 | 0.111 |
| Toluene               | 0.00 | 0.00  |
| Carbontetrachloride   | 0.00 | 0.00  |
| Ethyl methyl ketone   | 45.0 | 0.818 |
| Ethyl acetate         | 99.9 | 999   |
| Hexane                | 0.00 | 0.00  |
| Methyl isobutylketone | 62.0 | 1.631 |

ent tem per a tures from 303 K to 333 K and it was found that the ex trac tion of plat i num de creases as the tem per a ture in creases. The plots of log D against  $1/T \times 1000$  (K) are shown in Fig. 2. The  $\Delta$ H (change of enthalpy) are -6.565 kJ mol<sup>-1</sup> for ATTrespectivelyindicating exothermic reaction.

#### Effect of reagent concentration

Various volumes of 0.1% re agent so lu tion were added to the sam ple so lu tion con tain ing 0.5 mL of plat i num (stock so lu tion 0.1 mg/mL) at the re spec tive pH values. The absorbances re mained con stant when the volume of the re agent solu tion used was more than 0.5 mL. There fore 0.5 mL of 0.1%con centra tion of the re agent was sufficient for com plete quantitative extraction of the plat i num metal ion present in the aque ous phase. The ra tio of [ATT]/[Pt(IV)] was 10:1.

#### Ef fect of salt ing out agents

The presence of 0.1 M ni trate salts of al kali and al kaline met als such as Na, K, Mg, Ca, and Ba does not show any improve ment over the absorbance value of Pt:ATT ex tract (see Table 2).

#### Nature of extracted species

The na ture of ex tracted spe cies was as cer tained from the plot of log D vs log R from aque ous me dia Fig. 3, where

| Table 2. | Effect of | Salting | out 4 | Agent   | on | Pt:ATT | 'Com | plex |
|----------|-----------|---------|-------|---------|----|--------|------|------|
|          |           | ·····   |       | · · · · |    |        |      |      |

| Nitrate salts | Absorbance at 400 nm |  |  |
|---------------|----------------------|--|--|
|               | 0.312                |  |  |
| Barium        | 0.312                |  |  |
| Calcium       | 0.312                |  |  |
| Potassium     | 0.312                |  |  |
| Magnesium     | 0.312                |  |  |
| Sodium        | 0.312                |  |  |

log D is the distribution coefficient of the complex and log R is the concentration of reagent. The slope of the graph is 2.1409 for ATT. Thus the stoichiometry ratio of metal to reagent was found to be 1:2 with the reagent. The complex formation is through ion pair mech a nism. The prob a ble structure of Pt(IV) and ATT is proposed and the lone pair of electrons on ni trogen of the –SCN group and sul phur of thiophene play important roles in complex for mation.



#### Beer's law and sensitivity

A cal i bra tion graph for these met als was con structed under optimum conditions. The graph obeys Beer's law 5-120  $\mu$ g for plat i num. The mo lar ab sorp tivi ty and sandell sen si tivi ty were cal cu lated to be  $0.41 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup> and  $0.026 \ \mu$ g cm<sup>-2</sup>, respectively.



plex of Pt(IV) with ATT in ethyl ac e tate from aqueous media.

Table 4. Binary Separation of Pt(IV) with ATT in Ethyl Acetate from Aqueous Media

| Binary mixture    | Platinum found (ppm) |                 |  |  |
|-------------------|----------------------|-----------------|--|--|
| Metal taken (ppm) | Present method       | Standard method |  |  |
| Pt (5) + Mo (5)   | 4.98                 | 5.01            |  |  |
| Pt(4) + Cr(6)     | 4.01                 | 5.99            |  |  |
| Pt(6) + V(4)      | 5.99                 | 4.01            |  |  |
| Pt(5) + Zr(5)     | 4.98                 | 5.01            |  |  |

Each result is the average of three independent experiments.

# Influence of diverse ions on percentage extraction of Pt(IV)

Varying amounts of for eign ions were added in a fixed amount (100 µg) of plat i num(IV) to study the interference in the recommended extraction and subsequent determination procedure. The toler ance limit was set at the amount of foreign ions required to cause  $\pm 1.0\%$  error in the recommended procedure. The results are reported in Table 3.

# Separation of Pt(IV) from other precious metal ions

The proposed method facil i tates separation of platinum(IV) from its binary binary mixture with molybde num(II), chromium(II), zir conium(II), and vanadium(V). These metal ions do not extract and remain quantitatively in the aque ous phase under the optimum extraction conditions

Table 5. Masking Agents Required to Suppress the Interference of Foreign Ions

| Sr.No | Interfering Ion | Masking Agents Added |
|-------|-----------------|----------------------|
| 1     | Cu(II), Ni(II)  | Sodium thiosulphate  |
| 2     | Pd(II)          | Thiourea             |
| 3     | Fe(III)         | Thiourea             |
| 4     | Ce(IV), U(VI)   | Sodium fluoride      |
| 5     | Cr(III)         | Ammonium acetate     |

Table 3. Effect of Diverse Ions on Percentage Extraction of Pt(IV) with ATT in Ethyl Acetate from Aqueous Media. Pt(IV) = 100 µg

| Foreign ion        | Amount tolerable in mg | Foreign ion                                       | Amount tolerable in mg | Foreign ion        | Amount tolerable in mg |
|--------------------|------------------------|---|------------------------|--------------------|------------------------|
| Li(I), Na(I), K(I) | 25                     | F <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> | 10                     | Acetate            | 10                     |
| Ca(II)             | 25                     | $NO_2^{-}, NO_3^{-}$                              | 10                     | $CI$ , $SO_4^{-2}$ | 25                     |
| Mn(II)             | 10                     | $\text{ClO}_3^-, \text{IO}_3^-$                   | 10                     | Cynate             | 10                     |
| Ba(II)             | 10                     | BrO <sub>3</sub> <sup>-</sup>                     | 10                     | As(III)            | 10                     |
| Sr(II)             | 25                     | $SO_3^{-2}$                                       | 10                     | Bi(III)            | 10                     |
| Tartarate          | 10                     | $S_2O_8^{-2}$                                     | 10                     | Al(III)            | 10                     |

| Table 6. | Determination | of Pt(IV) | from Real | Samples |
|----------|---------------|-----------|-----------|---------|
|----------|---------------|-----------|-----------|---------|

| Standard samples     | % Present       | % Found          | % Recovery       | R.S.D              |  |
|----------------------|-----------------|------------------|------------------|--------------------|--|
| Cisplatin<br>Pt-wire | 65.0%<br>99.90% | 64.89%<br>99.81% | 99.83%<br>99.90% | $0.0408 \\ 0.0407$ |  |

Each result is the average of three independent experiments.

of plat i num(IV) with the ATT system facili tating separation of bi valent plat i num quant it a tively by the proposed method; the re sults are in Ta ble 4. The effect of some common tran sition metal ions was studied and their in terfer ence was masked by us ing proper mask ing agents (see Ta ble 5). It was observed that the Zn(II), Zr(II), Th(IV), Ag(I) metal ions do not in terfere in the process of extraction.

The proposed method also facil i tates determining plat inum(IV) from plat i num wire and cisplatin in jec tion (see Table 6). The con fi dence limit for 95% was cal cu lated and for cisplatin it was  $\pm 0.06\%$  and for plat i num wire  $\pm 0.1\%$ .

#### CONCLUSION

The re sults ob tained show that newly syn the sised ATT in ethyl ac e tate can be ef fec tively used for quan ti ta tive extrac tion of Pt(IV) from aque ous me dia. The pro posed method is quick and re quires less amount of or ganic sol vent. There are very few re agents which ex tract Pt(IV) from aque ous media which do not re quire the use of SnCl<sub>2</sub>. The equi lib rium time re quired is very short, i.e. only 1 min. and the com plex is sta ble for 72 hrs. The method has a de tect able range from 5-120  $\mu$ g for plat i num. The re sults show good agree ment with the stan dard method. The method is very pre cise.

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#### **Key Words**

Extraction; Platinum(IV); 2-Acetyl thiophenethiocynate; UV-spectrophotometer; Separation.

# Nomenclature:

D=Distribution ratio. % R=Per cent age re covery. aq. = Aque ous phase. org. = Or ganic phase. s = Sec ond. h = Hours <Subscripts>

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