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Short Communication

Selective spectrophotometric determination of micro amounts of palladium and osmium

BANI ROY, R. P. SINGH AND A. K. SINGH*
Department of Chemistry, University of Delhi, Delhi 110 007, India

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Abstract

In a strongly acidic medium 1-(α-naphthyl)-4,4,6-trimethyl-1H, 4H-pyrimidine-2-thiol (NTPT) forms chloroform-extractable yellow (λ_{max} 430 nm) and blue (λ_{max} 590 nm) coloured complexes (metal to ligand ratio 1 : 2) with palladium(II) and osmium(IV) respectively. Based on this, extractive spectrophotometric procedure for the determination of these metals separately and simultaneously was developed. Large excesses (at least 70–80 fold) of transition and other platinum metals do not interfere in the determination of both the metals.

Key words : 1-(α-naphthyl)-4,4,6-trimethyl-1H, 4H-pyrimidine-2-thiol palladium, osmium, determination.

1. Introduction

1-(α-Naphthyl)-4,4,6-trimethyl-1H,4H-pyrimidine-2-thiol (NTPT) is synthesised and used for the spectrophotometric determination of micro amounts of palladium and osmium. The results are reported in the present paper. The reagent is advantageous than other pyrimidine-2-thiols[1-3] as it can also be used for the determination of each of these metals in the presence of large quantities of the other.

2. Experimental

2.1. *Synthesis*[4] *and properties of NTPT*

A solution of 3·6 g α-naphthylamine in ethanol was added to a vigorously agitated mixture of 3·5 g 2-methyl-2-thiocyano-4-pentanone[4], 150 ml water and 5 ml concen-

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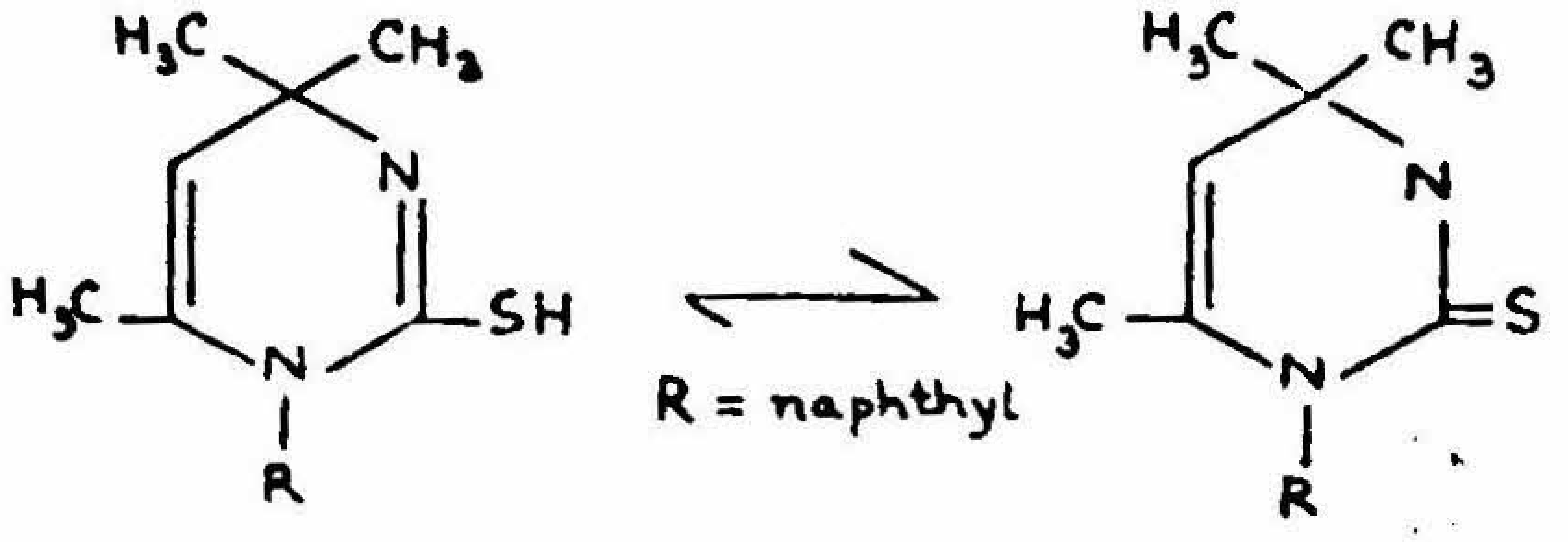
* M.D. University, Rohtak 124 001, India.

trated hydrochloric acid. The mixture was refluxed on an oil bath for 2 hr (approx.) and cooled to room temperature. NTPT, precipitated as white solid, was filtered; after 2–3 recrystallisations from acetone the m.p. was 220° C. Calculated: C, 72·30%; H, 6·38%; N, 9·98%; found C, 72·57%; H, 6·80%; N, 9·56%.

NTPT is insoluble in water and alcohol and sparingly soluble in acetone and benzene. However, it is highly soluble in chloroform (80 g/l) and moderately soluble in carbon tetrachloride.

Infrared spectra were obtained in KBr. It consists of a weak and broad band at 3175 cm^{-1} due to ν_{N-H}. No band corresponding to ν_{SH} is observed. However, a strong band due to $\nu_{C=S}$ occurs at 1175 cm^{-1}. This reveals that NTPT exists predominantly in the thio-keto form[8] which is a general characteristic of pyrimidine-2-thiols.



(thiol form) (thio-keto form)

The ultraviolet spectrum of NTPT taken in chloroform has maxima at 285 nm ($\epsilon = 1 \cdot 28 \times 10^4$ l mole^{-1}cm^{-1}) and 247 nm ($\epsilon = 1 \cdot 9 \times 10^4$ l mole^{-1} cm^{-1}).

2.2. *Palladium(II), osmium(VIII) and NTPT solutions*

Standard solutions of Pd(II) and Os(VIII) were prepared by dissolving appropriate amounts of anhydrous palladium chloride and osmium tetraoxide in 1·0 M hydrochloric acid and 1·0 M sodium hydroxide respectively. The palladium solution was standardised gravimetrically by precipitation of palladium as the dimethylglyoxime complex. The osmium solution was standardised iodometrically[6]. Os(IV) solution was obtained by acidification of the above solution with hydrochloric acid (final concentration 1·0 N).

The 0·01 M solution of NTPT was prepared by dissolving an appropriate amount of the reagent in freshly distilled pure chloroform., It was stable for several weeks.

All other chemicals used were of reagent grade. Doubly distilled water was used throughout the work.

2.3. *Apparatus*

Unicam SP 600 and Beckman DU-2 spectrophotometers were used for measuring absorbance in the visible and UV regions respectively. Infared spectra were recorded on a Perkin-Elmer 621 spectrophotometer.

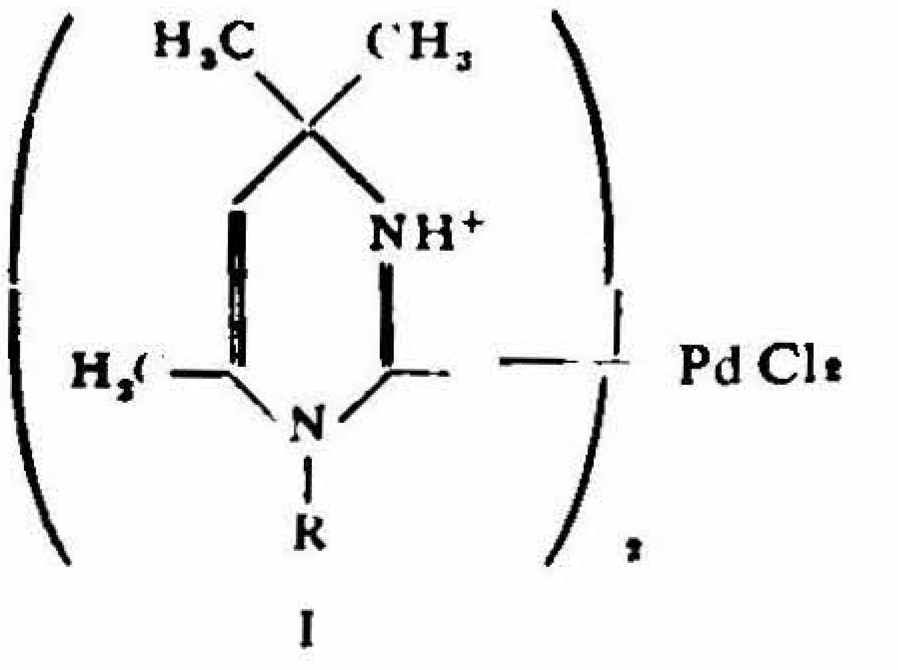
2.4. *Procedure for determination*

Adjust the acidity of a suitable aliquot (Table I) of palladium(II) or osmium(IV) solution and make its volume up to 10 ml with double distilled water. Shake it with 10 ml solution (0·01 M) of NTPT in chloroform for 15 and 25 min respectively for palladium and osmium on an electric shaker. Separate the organic phase, centrifuge and measure its absorbance at λ_{max} of the complex against the chloroform blank. Deduce the metal content from the calibration graph.

3. Results and discussion

3.1. *Reaction of NTPT with palladium(II) and osmium(IV)*

When a colourless solution of NTPT is shaken with acidic solutions of palladium(II) and osmium(IV), yellow (λ_{max} 430 nm) and blue (λ_{max} 590 nm) complexes are passed into organic phase respectively. The complexes can also be extracted if benzene, carbon tetrachloride and *n*-butanol are used in place of chloroform, but the absorbances of extracted complexes have been found to be maximum in chloroform. Characteristics of these complexes are summarized in Table I. The probable structures of the complexes are I and II.



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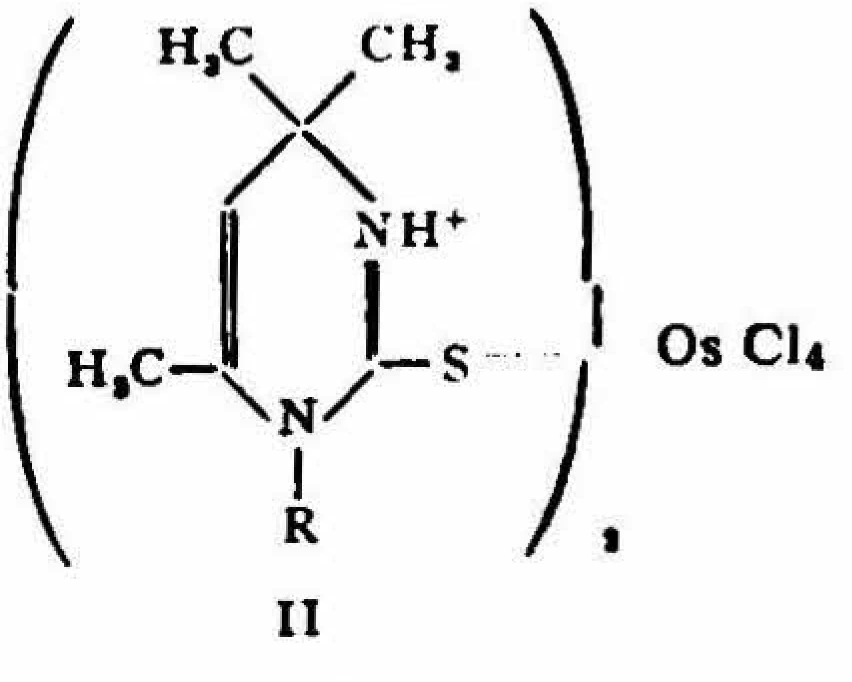

II

NTPT is acting as monodentate ligand because coordination through ring N will give unstable 4-membered ring. In highly acidic medium the complexation of enol form and protonation of the complex is most likely. To adjust acidity, other mineral acids, *viz.*, sulphuric, nitric, perchloric and phosphoric acids can also be used. Osmium cannot be extracted from media having acid concentrations below 4N.

3.2. *Effect of foreign ions*

Tolerance limits (μg/ml) of diverse ions in the determination of 12·8 μg/ml of palladium and 19·02 μg/ml of osmium are given (see p. 16) in the parentheses following them. Cyanide and thiourea must be absent as they cause serious interferences,

Table I

Characteristics of palladium and osmium complexes with NTPT

Characteristic	Complex	
	Palladium	Osmium
ϵ_{max} l mole^{-1} cm^{-1}	$3 \cdot 9 \times 10^3$	$4 \cdot 3 \times 10^3$
Reagent ratio for full colour development	20	25
Shaking time for complex extraction	15 min	25 min
Medium for maximum absorbance	0·4–9 N HCl	5–6 N HCl
Beer's law upper limit µg/ml	34	39
Accurate range for determination µg/ml	4–26	6–38
Metal : ligand ratio*	1 : 2	1 : 2
Sandell's sensitivity µg/cm^2	0·033	0·045
Standard deviation** (from 6 samples)	0·0049	0·0068

* Determined by Job's method.

** Of the absorbance for 12·8 µg/ml palladium and 19·02 µg/ml osmium.

Palladium : F^-, Br^-, NO_3^- (8×10^3); CH_3COO^-, PO_4^{3-}, BO_3^{3-} (5×10^3); citrate $(1 \cdot 5 \times 10^3)$; $C_2O_4^{2-}$ (2×10^3); EDTA, tartrate (1×10^3); I^- (400); NO_2^- (500); SCN^- (500); $S_2O_3^{2-}$ (50); Ba^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+} (8×10^3); Pb^{2+} $(2 \cdot 5 \times 10^3)$; V^{4+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} (2×10^3); Fe^{3+}, Sn^{4+} (10^3); Ru^{3+}, Ir^{3+} $(7 \cdot 5 \times 10^3)$; Rh^{3+} (6×10^3); Pt^{4+} $(4 \cdot 5 \times 10^3)$; Ag^+ (10); Os^{8+} (8×10^3)*.

Osmium : F^-, NO_3^-, Br^-, SO_4^{2-}, acetate $(4 \cdot 5 \times 10^3)$; PO_4^{3-} BO_3^{3-}, $C_2O_4^{2-}$ (2×10^3); tartrate, EDTA (10^3); citrate $(1 \cdot 5 \times 10^3)$; I^- (200); $S_2O_3^{2-}$ (100); NO_2^- SCN^- (50); Ca^{2+}, Ba^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+} (4×10^3); Al^{3+}, Cu^{2+} (2×10^3); Fe^{3+}, Co^{2+}, Ni^{2+}, V^{4+}, Mn^{2+} (10^3); Pb^{2+} $(4 \cdot 5 \times 10^3)$; Hg^{2+} (2×10^3); Sn^{4+} (5×10^2); Pt^{4+} $(1 \cdot 5 \times 10^3)$; Rh^{3+}, Ir^{3+} (10^3); Ru^{3+} (2×10^3); Ag^+ (15).

Up to 500 µg/ml of palladium can be tolerated if following modified procedure is used for the determination. To a suitable aliquot of mixture of palladium and osmium add 5N HCl so that the final solution (total volume 10 ml) is 1N with respect to acid. Shake it with sufficient amount of NTPT solution in chloroform for 15–20 min. Separate the aqueous phase, adjust its acidity level to 5–6 N hydrochloric acid and add 10 ml 0·01 M NTPT solution in chloroform. Shake for about 25 min, separate the organic phase and measure its absorbance at 590 nm against chloroform blank.

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* At acid concentration < 4N.

The palladium content of the mixture can also be determined by measuring the absorbance of the first extract at 430 nm. Results of the analysis of binary mixtures containing osmium and palladium are given in Table II.

Table II

Determination of palladium and osmium in binary mixtures

Palladium present µg/ml	Palladium found µg/ml	Standard deviation	Osmium present µg/ml	Osmium found µg/ml	Standard deviation
12·80	12·78	0·0069	19·02	18·90	0·0068
5·33	5·10	0·0068	19·02	19·00	0·0076
12·80	12·60	0·0075	9·51	9·40	0·0069
25·60	25·50	0·0069	9·51	9·42	0·0075
6·40	6·26	0·0069	19·02	19·00	0·0075

3.3. *Simultaneous determination of palladium and osmium*

Difference of 160 nm in the λ_{max} of the two complexes and the fact that the absorbance of each complex at the λ_{max} of the other one is small, make the applicability of Sandell's equation[6] for simultaneous determination of palladium and osmium possible. Results are given in Table III.

3.4. *Determination of palladium and osmium in ores and alloys*

On account of the difficulty in getting the naturally occurring ores of osmium and palladium, and their alloys, synthetic mixtures having the same composition (corresponding to ores and alloys) were analysed for these two metals by using the above mentioned procedures. The results are incorporated in Table IV.

3.5. *Comparison with other reagents*

Photometric reagents[6,7] of attractive sensitivities, *e.g.*, iodine, dithizone, α-furildioxime and pyridine—Rose Bengal for palladium and diphenylcarbazide and 1-naphthyl amine-4, 6, 8-trisulphonic acid for osmium usually suffer from serious interferences and necessity of rigid control over working conditions. NTPT, though inferior in sensitivity in comparison, is far superior in selectivity as no other platinum metal interferes in the

Table III

Simultaneous determination of palladium and osmium in synthetic mixtures

Palladium taken µg/ml	Osmium taken µg/ml	Palladium found µg/ml	Standard deviation	Osmium found µg/ml	Standard deviation
12·80	19·02	12·76	0·0050	19·21	0·0045
5·33	19·02	5·00	0·0050	19·03	0·0040
12·80	9·51	12·85	0·0055	9·70	0·0050
25·60	9·51	25·62	0·0045	9·60	0·0045
6·40	19·02	6·34	0·0045	19·04	0·0040

Table IV

Determination of palladium and osmium in synthetic mixtures corresponing to alloys and ores

Composition of mixture (µg/ml)	Palladium found µg/ml	Standard deviation	Osmium found µg/ml	Standard deviation
Os(20) ; Ir(44) ; Ru(4·4) ; Pd(5·6)	5·4	0·0098	19·89	0·0102
Os(20·57) ; Ir(5·24)* Ru(2·75) ; Pt(0·06)	..	..	20·53	0·0068
Os(16·48) ; Ir(4·0)* Ru(2·09) ; Pt(0·045)	..	..	16·47	0·0076
Os(19·83) ; Ir(4·82)* Ru(2·52) ; Pt(0·065)	..	..	19·80	0·0076
Ru(0·396) ; Pd(9·52)**	9·50	0·0069	..	..
Pt(5) ; Pd(5)**	4·86	0·0069	..	..

* Corresponding to osmiridium or syserkite.

** Corresponding to Ru–Pd or Pt–Pd alloy.

determination. Moreover, the procedure is simple and rapid. Separation and simultaneous determination of the two metals is also possible with the reagent which cannot be done with other pyrimidine-2-thiols[1-3].

When additional steps (masking agents and separation procedures) are not to be introduced, and whenever high sensitivity is not required, colorimetric methods involving dimethylglyoxime (DMG) for palladium and thiourea for osmium are most suitable of those proposed to date. The present reagent (NTPT) is three times sensitive for palladium in comparison to DMG and as sensitive as thiourea for osmium with distinct advantages of higher selectivity, simplicity and wider applicability.

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