

Spectrophotometric Determination of Palladium (II) & Platinum (IV)

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Abstract: 2-Hydroxy-4-methoxy, acetophenonethiosemicarbazone is proposed as a new reagent for the spectrophotometric determination of palladium (II) and platinum (IV). At pH 6.0 Pd(II) forms an instantaneous 1:2 complex at room temperature and has maximum absorbance at 360 nm. Pt(IV) forms 1:2 complexes on heating with maximum absorbance at 360 nm. Both the complexes are stable and conform Beer's law. The molar absorptivities for Pd(II) and Pt(IV) complexes are 16950 and 140251 mol⁻¹ cm⁻¹ respectively. The proposed methods are suitable for the determination of Pd(II) or Pt(IV) in the presence of associated metal ions. The solid complexes are isolated and are characterized by various physicochemical techniques.

Keywords: Palladium(II) and Platinum(IV) determination; 2-Hydroxy-4-methoxyacetophenone thiosemicarbazone; spectro-photometry

1. Introduction

Thiosemicarbazones have been widely used as spectrophotometric reagents for the determination of metal ions and their analytical potentialities have been reviewed recently (Singh and Ishii 1991; Grag and Jain 1988). In continuation of our earlier work on the analytical applications of hydroxyacetophenone thiosemicarbazones (Murthy and Reddy 1992, 1989, 1989, 1988), we are now reporting the use of a new compound 2-hydroxy-4-methoxyacetophenone thiosemicarbazone (HMAPT) as a reagent for the spectrophotometric determination of palladium(II) and platinum(IV). Most of the spectrophotometric methods for palladium using thiosemicarbazones (Singh and Ishii 1991; Greg and Jain 1988) suffer from low sensitivity, need for heating or extraction and poor selectivity. The proposed method based on HMAPT is free from these drawbacks. The method is simple, rapid and was applied to the determination of Pd in a simulated solution of its alloy. For platinum only limited number of thiosemicarbazone methods are available (Singh and Ishii 1991; Grag and Jain 1988) and each method has its own disadvantages like extraction, slow colour formation and rigid experimental procedures. The method described herein overcomes all these difficulties such as simple, reasonably selective and sensitive.

2. Experimental

All the reagents and chemicals used were of AR grade. HMAPT was (m.p. 194-196°C) synthesized by the method reported earlier (Murthy and Reddy 1992) and its solution (5 x 10⁻²M) was prepared in DMF. Palladium(II) solution was prepared from PdCl₂ and standardized gravimetrically (Vogel 1908). Platinum(IV) solution was prepared from PtCl₄ and standardized gravimetrically (Dey 1961). The stock solutions are diluted as required. Hydrochloric acid -

sodium acetate (0.3 -3.5 pH) and sodium acetate - acetic acid (3.5 - 6.5 pH) buffers were used in the present study.

A spectronic- 21, Bausch-Lomb spectrophotometer and an ELICO pH meter of model LI-120 were used for absorbance and pH measurements.

2.1. Recommended Procedure

Samples were prepared in a 25mL calibrated flasks by taking 12.5 mL of buffer solution (Pd, pH 6.0; Pt, pH 2.5), 6 mL of DMF, known volume of the sample solution containing 0.21-6.36 ppm of Pd(II) or 0.39-11.70 ppm of Pt(IV) and 0.5 mL of 5 x 10⁻²M HMAPT solution in DMF and diluted to volume with distilled water. For Pd(II), the absorbance was measured at 360nm against a reagent blank. For Pt(IV) the reaction mixture was heated on a boiling water bath for 30 min and was cooled to room temperature (30 ± 5⁰ C). The absorbance of the solutions was measured at 360 nm against a reagent blank prepared under identical conditions. The amount of Pd(II) or Pt(IV) was deduced from the respective calibration graphs (Fig. 1 & 2).

3. Results and discussion

The reaction between Pd(II) and HMAPT is instantaneous at room temperature, but with Pt(IV), the reaction is slow at room temperature and required heating. Maximum color development was observed on heating the solution to higher temperature on a boiling water bath for about 30 min. The presence of excess of DMF and the order of addition of constituents have no effect on the absorbance of the complexes. Some important physicochemical and analytical properties of the complexes are given in the Table 1.

The effect of some foreign ions which often accompany Pd(II) or Pt(IV) was studied by adding different amounts of diverse ions. The following amounts (in - fold excess to Pd or Pt) of foreign ions are found to give Less than ± 2% error

in absorbance reading in the determination of 3.18 ppm of Pd(II) or 5.85 ppm of Pt(IV) respectively. In the determination of Pd(II) and Pt(IV) respectively, Phosphate and bromate (175); tetraborate and tartrate, sulphate, oxalate (100); chloride, perchlorate, fluoride, oxalate, Cd(II) and oxalate, chloride, phosphate and citrate (70); nitrate, Mg(II) and thiocyanate, iodide (45); thiourea, Th(IV), Mo(VI) and thiosulphate, EDTA (25); U(VI), W(VI) and fluoride, Ce(IV), W(VI) (15); Mn(II), Ag(I) and fluoride, tetraborate, bromate, U(VI), Ce(IV), W(VI), Cd(II), Mo(VI), Mn(II), (10); Al(III) and Ag(I), Th(IV) (3); Ce(IV) and Mg(II) (2); did not interfere. However, equal amounts of Cr(III), Pt(IV) and ascorbic acid, V(IV), V(V), Ni(II) did not interfere in palladium and platinum methods respectively. In both the cases small amounts (Less than Pd) of Ru(III), Cu(III), Co(II), Au(III) and Ru(III), Pd(II), Au(III) (less than Pt) are tolerated. In the case of palladium complex 480, 375, 250, 160 fold excess of citrate, tartrate, sulphate, iodide is found to be tolerable. However, the interference due to a 3, 10, 70 and 10 fold excess of V(IV or V), Ni(II), Zn(II) and Pt(IV) could be removed by masking these ions with citrate and EDTA respectively. Fe(III) interferes and 10-fold excess could be eliminated by phosphate.

The method developed for Pd(II) or Pt(IV) was applied to the determination of palladium or platinum in a simulated sample of its alloy. The results are presented in the Tables 2 and 3 respectively.

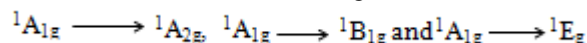
The preparation of the complexes in solid state, a hot aqueous solution of the metal salt was added dropwise to a hot solution of the reagent in aqueous buffer solution of desired pH (Pd-6.0; Pt-2.5), until the required metal to ligand ratio is reached. The solid which is separated after

refluxion for 3 h was filtered and washed with hot water, and then with ethanol and dried at 80°C in an electric oven.

The analytical data of the complexes are in good agreement with the proposed molecular formulae (Table 4). Both the complexes are insoluble in common organic solvents but soluble in DMF and DMSO. The complexes are non-hygroscopic and are found to be stable in atmospheric air.

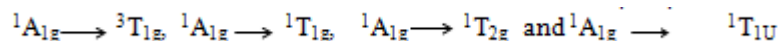
The IR (KBr discs) spectral data showed that the $>C=N$ (Singh et al 1988) and $>C=S$ (Laxmi Bhal et al 1983) modes shifted from 1620 and 1045 cm^{-1} in the HMAPT ligand to 1600 and 1035; and 1600 and 1015 cm^{-1} in the palladium and platinum complexes respectively, indicating the involvement of the $>C=S$ and groups in coordination. The Pd-N, Pd-S and Pt-N, Pt-S bands (Sahni et al 1978) appeared around 440, 390 and 505, 400 cm^{-1} respectively in the complexes conforming the above fact. The bands observed at 340 and 350 cm^{-1} are assigned to Pd-Cl and Pt-Cl vibrations respectively (Sahni et al 1978).

The electronic spectrum of the Pd(II) complex displayed three bands at 16390, 25680 and 29815 cm^{-1} , which are similar to those observed for other palladium complexes of thiosemicarbazones and are assigned to the transitions.



respectively indicating a square planar geometry for the complex (sahni et al 1978). The diamagnetic nature of the complex also supports this stereochemistry.

The electronic spectrum of Pt(IV) complex showed bands at 19800, 31250, 34300, 37820 cm^{-1} . These bands are assigned to



transitions respectively and are indicative of octahedral geometry for the complex (Sahni et al 1978). This assignment is also supported by the diamagnetic nature of the complex.

The molar conductivity measurements of the complexes in DMF showed both the complexes to be neutral. On the basis of the above data, structure I and structure II may be assigned to Pd(II) and Pt(IV) complexes respectively.

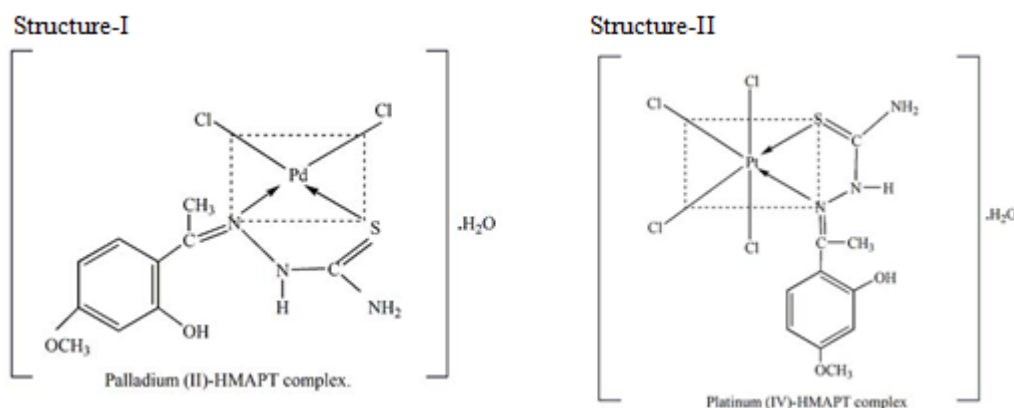


Table 1: Physicochemical. & analytical properties of the complexes

S.No	Characteristic	Complexes	
		Pd	Pt
1	Colour	Yellow	Yellow
2	λ_{\max} (nm)	360	360
3	Optimum pH range	6.0 - 7.0	2.0 – 3.0
4	Mole of reagent required per mole of metal	5	5
5	Time stability	10h	10h
6	Beer's law validity range (ppm)	0.21 - 6.36	0.39 – 11.70
7	Optimum concentration range (ppm)	1.27 – 6.28	2.34 – 11.45
8	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$	16950	14025
9	Sandell's sensitivity $\mu\text{g cm}^{-1}$	0.0063	0.0139
10	Composition of the complex ^a (M:L)	1:2	1:1
11	Stability constant of the complex ^b	1.47×10^8	2.04×10^4
12	Standard deviation ^c	0.0148	0.0108
13	DMF percentage	26	26

^aDetermined by Job's and molar ratio methods^bDetermined by Job's method.^cFor ten replicate determinations**Table 2:** Determination of Palladium in a simulated sample of its alloy

S.No	Simulated sample composition (%)	Amount of Pd (ppm)		Error (%)
		Taken	Found*	
1	Pd 10.5, Ni 60.0	1.68	1.66	1.19
2	Pt 20.0, V 9.5	1.89	1.90	0.53
		2.10	2.13	1.43

*Average of three determinations

Table 3: Determination of Palladium in a simulated sample of its alloy / Catalyst solutions

S.No	alloy / Catalyst	Amount of Pd (ppm)			Error (%)
		Platinum taken	Metal ion added	Platinum found*	
1	Pt – W alloy (Pt 95.2%, W 0.8%)	2.80	W 0.13	2.76	1.43
		5.60	W 0.25	5.64	0.71
		8.40	W 0.34	8.38	0.24
		10.00	W 0.51	10.04	0.40
2	Binary catalyst (Pt 27.3%, Al 72.7%)	1.56	Al 4.20	1.54	1.28
		3.12	Al 8.30	3.15	0.96
		4.68	Al 12.50	4.73	1.07

* Average of three determinations

Table 4: Analytical & physical data of solid complexes

S.No	Complex	Colour	Found (calc) %					μ_{eff} (B.M)	Molar conductance (Ohm cm^2/mol)
			C	H	N	S	M		
1	Pd HMAPT Cl_2	Brown	27.10 (27.57)	3.91 (3.70)	9.58 (9.65)	7.14 (7.36)	24.29 (24.42)	Diamagnetic	9.40
2	Pt HMAPT Cl_4	Brown	20.0 (20.17)	2.70 (2.71)	7.03 (7.06)	5.26 (5.38)	32.78 (32.75)	Diamagnetic	18.40

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