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1,3-Cyclohexanedione bisthiosemicarbazone monohydrochloride as a chromogenic reagent for the rapid spectrophotometric determination of platinum; physicochemical date of platinum complex

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Abstract

1,3-Cyclohexanedione bisthiosemicarbazone monohydrochloride (1,3-CHDT.HCl) reacts with platinum (IV) in sodium acetate-acetic acid buffer to form yellowish-green coloured 1:1 (M:L) complex having absorbance maximum at 375 nm. Beer's law is valid over the concentration range 0.78 - 18.73 ppm. The molar absorptivity and Sandell's sensitivity of the method are 1.0×10^4 litre mol^{-1}. cm^{-1}. and 0.0195 $\mu g\,cm^{-2}$ respectively. The effect of pH, time, concentration of reagent, order of addition of reagents and influence of foreign ions are reported. Synthetic samples whose composition correspond to dental alloy are analysed for the determination of platinum. The solid complex (1:1) formed by Pt(IV) and 1,3-CHDT.HCl is isolated and characterized on the basis of elemental, magnetic susceptibility, thermal and infrared spectral analysis.

Key words: Spectrophotometry, platinum (IV), 1,3-cyclohexanedione bisthiosemicarbazone monohydrochloride.

1. Introduction

Several reagents have been suggested[1] for the spectrophotometric determination of platinum. Methods available are dependent upon various factors such as temperature (heating of reaction mixture for longer or specified time)[2-8], time[9], concentration of reagent and certain foreign ions[4-9]. The present method offers the advantage of simplicity, rapidity, reasonable selectivity without the need for heating or extraction. 1,3-CHDT.HCl has been used for the spectrophotometric determination of chlorate[10], bromate[11], iodate[11], bismuth[12], palladium[13], nickel[13] and chromium[14]. 1,3-CHDT.HCl is water soluble reagent and can be used with advantage.

2. Experimental

ECIL spectrophotometer Model GS 865 A and ELICO pH meter Model LI-120 were employed in the present study. Magnetic susceptibility measurements were made at room temperature by standard Guoy method using mercury tetrathiocyanato cobaltate (II) as calibrant ($\chi g = 16.44 \times 10^{-6}$ C.G.S. units). The IR spectra in the range 4000 - 200 cm^{-1} was recorded on a Perkin Elmer 983 IR spectrophotometer in KBr medium. Thermal decomposition study was made using a Stanton Thermobalance Model HI-SM with a heating rate of 6° min^{-1}.

1,3-CHDT.HCl was prepared according to the procedure given in literature[15] and the reagent (2×10^{-2} M) solution was prepared in distilled water.

A stock solution of platinum was prepared by dissolving a known weight of platinum wire (99.99% pure) in hot aqua regia and the solution was evaporated to a small volume. The residue was treated with 5 ml of conc. hydrochloric acid and evaporated to a small volume. This treatment was repeated five times in order to destroy any nitroso complexes formed. The residue from final evaporation was then dissolved and diluted to 100 ml with 1 M hydrochloric acid. Solutions of lower concentrations were obtained by dilution with water as required.

Hydrochloric acid (1 M) + sodium acetate (1 M) (pH 0.5 to 3.0) and sodium acetate (0.2 M) + acetic acid (0.2 M) (pH 4 to 6.5) buffers were used in the pH metric study.

All other reagents used were of analytical grade.

3. Recommended procedure

To a suitable aliquot containing 0.8-18 ppm of platinum in a 25 ml volumetric flask, add 10 ml of buffer (pH 4.0), 2.5 ml of dimethylformamide and 3 ml of 2×10^{-2} M 1,3-CHDT.HCl solution. Dilute the solution up to the mark with distilled water. Measure the absorbance after 20 minutes at 375 nm against a reagent blank prepared under identical conditions. Construct the calibration graph similarly. The concentration of platinum in the sample is calculated using the calibration graph.

4. Results and discussion

The order of addition of the constituents (metal ion, buffer and reagent) has no effect on the absorbance. The complex formation is quite rapid and the complex is stable for 12 hours in the presence of 10% dimethylformamide. Effect of time on absorbance in presence of different amounts of dimethylformamide indicates that the complex attains maximum absorbance in the presence of 4-32% DMF after a period of 20 min. In the absence of dimethylformamide, turbidity, due to the precipitation of complex, is observed which causes a rapid increase in the absorbance. The complexation reaction was studied in detail with a view to finding optimum conditions for the estimation of platinum. The important analytical characteristics are summarised below. pH range 2.5-5.0; λ_{max} 375 nm; Mole of reagent required per mole of metal ion for full colour development, 20; Beer's law validity range, 0.78-18.73 ppm; Optimum concentration range, 4.7-14.0 ppm; Molar absorptivity, 1.0×10^4 litre $mole^{-1}$. cm^{-1}; Sandell's sensitivity 0.0195 μg of Pt (IV) cm^{-2}; Composition 1:1 (metal: ligand as determined by Job's and mole ratio methods); Stability constant 3.0×10^9. Standard deviation for ten replicate determinations of 6.2 ppm of platinum, 0.0018. A comparison of spectrophotometric reagents[16-25] for the determination of platinum is given in Table I.

Table I
Comparison of spectrophotometric reagents for the determination of platinum

Reagent	Molar absorptivity lit. $\text{mol}^{-1}.\text{cm}^{-1}$.	Medium	Comments heating/ time	Interference due to	Ref
1,3-CHDT. HCl	1.0×10^4	Aqueous	20 min. time for colour development	Ag	
Thiosalicylamide	1.2×10^3	$CHCl_3$	—	Fe, V and Os	16
1-(2-pyridylazo)-2-naphthol	4.9×10^3	$CHCl_3$	Heating for 30 min. at 100°C	Fe and Au	17
Benzil α-monoxime	6.6×10^3	$CHCl_3$	Heating for 90 min. at 100°C	Ni, W, Th, Zr Al, Cu, Os, Rh and Fe.	7
Mapazine hydrochloride	1.4×10^4	Aqueous	—	Pd, Au, Ru and Fe	18
Phthalimide dithiosemicarbazone	1.5×10^4	Aqueous	Heating at 85°C for 60 min.	Cu, Pd, Ni and Au	4
Thiotropolone	1.9×10^4	$CHCl_3$	60 min. time for colour development	Fe, Co, Ni, Pd, and Ru	19
2,2'-dithiodianiline	1.9×10^4	Aqueous	10 min. time for colour development	Pd, Ru and Os	20
Thiosalicyloyl hydrochloride	2.7×10^4	$CHCl_3$	Heating for 15 min. at 100°C	—	21
1,4-Diphenyl thiosemicarbazide	2.8×10^4	Aqueous	Heating for 15 min. at 100°C	Au, Te and Ir	22
Chlorosulfophenol azorhodamine	3.2×10^4	Aqueous	4 hr time for colour development	Pd and Au	9
Benzoin-α-oxime	4.1×10^4	Aqueous	Heating for 30 min. at 100°C	Co, Fe, Ru, Os Zr and W	6
p-Nitroso-dimethylaniline	5.6×10^4	Aqueous	Heating for 90 min. at 87°C	—	23
Mercaptoacetanilide	9.56×10^3	$CHCl_3$	—	Ru, Rh, Fe, Os and Ir	24
Propionyl promazine phosphate	5.95×10^3	Aqueous	15 min. time for colour development	Ru, Os and Fe	25

4.1 Effect of foreign ions

The effect of foreign ions which often accompany platinum was studied with 4.7 ppm of platinum. Tolerance limit was taken as the amount of foreign ion required to cause ± 2% error in absorbance. Tolerance limit of various ions are presented in Table II, which indicates that platinum can be selectively estimated in the presence of large excess of many anions and cations.

4.2 Determination of platinum in synthetic samples

Synthetic samples whose composition correspond to dental alloy was analysed for the platinum determination (Table III). The recovery of platinum in presence of higher amounts of uranium and other platinum group metals was also studied (Table IV). Ascorbic acid (250

Table II

Effect of foreign ions on the determination of 4.7 ppm of platinum

Ion added	Tolerance limit (ppm)	Ion added	Tolerance limit (ppm)
Fluoride	760	Te (II)	25
Chloride	5600	Mn (II)	440
Bromide	1280	Co (II)	24
Iodide	101	Ni (II)	50
Phosphate	760	Cu (II)	5
Nitrate	992	Zn (II)	261
Sulphate	1536	Pb (II)	40
Oxalate	528	Pd (II)	6*
Thiocyanate	116	Cd (II)	130
Thiosulphate	450	Fe (III)	220 †
Thiourea	364	Al (III)	216
Tetraborate	1210	Cr (III)	104
Citrate	1520	Ru (III)	5
Tartrate	2368	Rh (III)	6
Chlorate	396	Au (III)	4
Bromate	102	Au (III)	25 §
Iodate	7	Ir (III)	32
EDTA	1888	Zr (IV)	72
DMG	400	Ti (IV)	38
Hydroxylamine HCl	270	V (V)	4
Ascorbic acid	300	U (VI)	950
		Mo (VI)	4
		W (VI)	37
		Os (VIII)	8‡

* In the presence of 1800 ppm of EDTA

† In the presence of 700 ppm of fluoride

‡ In the presence of 300 ppm of thiourea

§ In the presence of 250 ppm of ascorbic acid

Table III
Analysis of synthetic sample whose composition corresponds to dental alloy †

Volume of sample (ml)	Amount of platinum		Error (%)
	Taken (ppm)	Found * (ppm)	
2	4.42	4.40	- 0.35
4	8.84	8.89	+ 0.56
6	13.26	13.35	+ 0.69

* Average of three determinations
† dental alloy composition —
Ag 38%, Au 27%, Pd 25%, Pt 15%,
Cu 4%, Zn 1%.

Table IV
Analysis of synthetic † sample

Volume of sample solution (ml)	Amount of platinum		Error %
	Taken (ppm)	Found * (ppm)	
2.0	4.68	4.64	- 0.4
3.0	7.02	7.20	+ 2.5
4.0	9.36	9.20	- 1.7
6.0	14.04	14.21	+ 1.2

* Average of three determinations
† Composition of synthetic sample solution
U, 117 ppm (82.64%); Ir, 11.7 ppm (8.26%); Os, 3.51 ppm (2.47%); Ru, 2.34 ppm (1.65%);
Pd, 2.34 ppm (1.65%) and Pt, 2.34 ppm (1.65%).

ppm), thiourea (300 ppm) and EDTA (1800 ppm) were added to mask gold, osmium and palladium respectively. Since silver is present in the dental alloy it gives precipitation by the addition of 1,3-CHDT.HCl. The precipitate was removed by filtration.

5. Synthesis and characterization of Pt-1,3-CHDT complex

A hot aqueous solution of platinum (IV) was added dropwise to a refluxing solution of ligand (which was mixed with buffer; pH 4.0) until the metal ligand ratio[26] reached 1 : 1. The solid which separated (after 30 min) was filtered after cooling the solution. The solid was washed with hot water and methanol and dried at 80°C for 1 hr in an electric oven.

Results obtained in elemental analysis, magnetic susceptibility measurements, thermal study, conductivity experiment and infrared spectral studies are presented in Table V. Infrared data for $\upsilon C = N$ and $\upsilon C = S$ suggest the participation of azomethine nitrogen

Table V

Physio-chemical data of the solid complex

Data	Value		Assignment
Elemental analysis	Found (calc.)		
Platinum %	32.71 (32.75)		Corresponds to
Sulphur %	10.81 (10.75)		$PtLCl_3$. 2 H_2O
Chloride %	17.79 (17.86)		
Magnetic susceptibility			
χ_g C.G.S. units	-0.85×10^{-6}		Diamagnetic
T.G. studies			
Temp (°C) range	Percentage of fraction weight Found (calc.)		
80 - 120	6.04 (6.00)		Loss of two water molecules
200 - 230	18.00 (17.80)		Loss of three chloride ions.
310 - 450	43.00 (43.30)		Loss of ligand
450 - 800	34.00 (32.70)		Remaining residue corresponds to Pt metal
Infrared spectra	Ligand	Complex	
Spectral bands in the region (γ ; cm^{-1})	3420-2920	3420-2920	NH and NH_2[29]
	1630 (s)	1600 (s)	C = N[28]
	1510 (s)	1510 (s)	$\gamma^{(CN)}$
	1095 (s)	1065 (m.s)	(C = S)[26]
Molar conductance (in DMF) (ohm^{-1} cm^{-2} mol^{-1})		141	Ionic nature of complex

atom[27,28] and thioketo sulphur[26] in chelation. The pK 1 and pK 2 values for reagent are 4.75 and 10.5 respectively[15] (buffer used in the present study is having pH 4.0). The reagent (I) loses one proton preferably from quarternary ammonium group at pH. 4.0 since pK 1 is 4.7 (II). The pK 2 value (10.5) of the reagent refers to the enolization of $> C = S$ group. The acid is neutralised on increasing the pH and the $> C = S$ bonds of ligand enolize (III) or dissociate in alkaline medium[15]. No colour reaction is observed between Pt (II) and reagent. Pt (IV) complexes are stable and known to form octahedral complexes. The expected molar conductance value for $[ML]\ Cl_3$ complex is not observed and the observed value (c.a 141) suggests the following structure of the complex (IV) in analogy with our previous observation[14].

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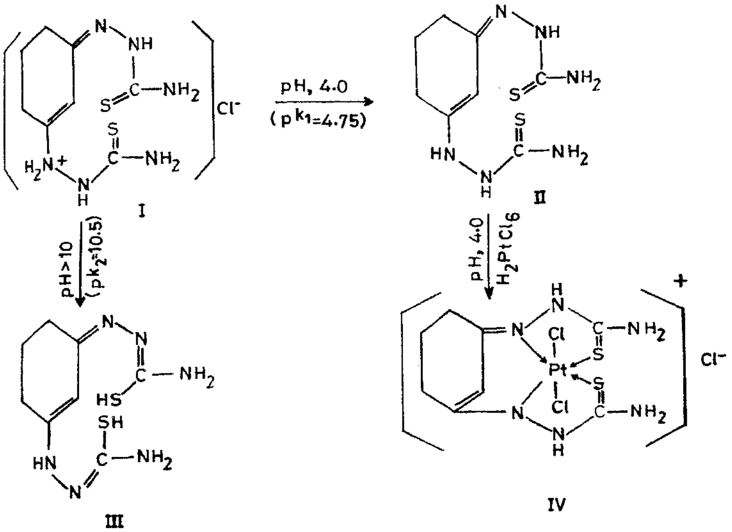

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