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Palladium Ternary Complex with Chromeazurol S and Cetyltrimethylammonium Bromide and Cetylpyridinium Bromide

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Formation of green coloured ternary complexes between palladium, chromeazurol S and cetyltrimethylammonium bromide or cetylpyridinium bromide is described over the pH range 4.6 to 5.6. The compositions, $Pd(CAS)CTA_2$ and $Pd(CAS)CP_2$ for the ternary complexes have been established by Job's method of continuous variations and by the mole ratio method using absorbance data. Strict control of experimental conditions is essential for employing these methods for the determination of composition. The ternary systems obey Beer's law between 0.053 to 2.98 ppm of palladium. A high molar absorptivity (Pd-CAS-CTAB, 5.25×10^4; Pd-CAS-CPB, 6.16×10^4 mol^{-1} cm^{-1}) and Sandell's sensitivity (0.002 μg cm^{-2}) have been obtained at 620 nm. A spectrophotometric method has been proposed using these ternary complexes for microdetermination of palladium. The method is sensitive, precise and selective. The effect of various cations and anions is studied. The mode of formation and structures of the ternary complexes are discussed.

A number of ternary complexes of cetyltrimethylammonium bromide (CTAB) and cetylpyridinium bromide (CPB) have been found useful for increasing the sensitivity, selectivity and molar absorptivity of molecular absorption spectroscopy[1–9]. This communication presents a detailed spectrophotometric study on the composition, stability and analytical applications of ternary complexes of palladium with chromeazurol S (trisodium salt of 3″-sulpho-2″ : 6′-dichloro-dimethyl-4 hydroxy fuchsone-5:5′-dicarboxylic acid abbreviated as CAS) and CTAB or CPB.

Palladium forms a binary chelate with CAS having λ_{max} at 590 nm[10]. On addition of suitable amounts of CTAB or CPB to this binary chelate in the pH range 4.6 to 5.6, a green ternary complex (λ_{max} 620 nm) is formed. The absorption spectra of these ternary complexes exhibit a bathochromic shift in the absorption maxima accompanied by at least a five-fold increase in absorbance leading to better conditions for spectrophotometric determination of palladium. The sensitivity and molar absorptivity value increase several-fold and only a limited number of cations interfere in the determination. It has been observed that strict control of experimental conditions is essential for

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establishing the composition of such ternary complexes. Conditional formation constant values have been calculated by a new simple method[1], especially useful in the case of outer-sphere complexes. On the basis of experimental results obtained, a method has been worked out for spectrophotometric determination of palladium. The method has been tested in the presence of several cations and anions. The tentative structures of the ternary complexes are also discussed.

EXPERIMENTAL

Reagents

A stock solution of CAS was prepared by dissolving the required amount in redistilled water. Palladium chloride solution was prepared by dissolving a weighed amount in aqua regia. This solution was evaporated to dryness. Sufficient HCl was added to the residue and the solution was evaporated to dryness. This process was repeated many times in order to remove the nitric acid. The residue was dissolved in a minimum volume of boiling water containing a few drops of dil HCl and then diluted with redistilled water. This solution was standardized by dimethylglyoxime as a precipitating reagent[11]. Solutions of CTAB and CPB were prepared by dissolving weighed amounts in hot redistilled water and were standardized by argentometric determination of bromide ion contents. Working solutions were prepared by appropriate dilution of stock solutions. Acetate buffer solutions (0.20 M) were used for maintaining the desired pH of the mixtures. All chemicals used were of analytical reagent grade.

Apparatus

Absorbance measurements were made with a Beckman DU spectrophotometer. A Leeds and Northrup direct reading pH indicator with a glass-calomel electrode system was employed for pH measurements.

Experimental Conditions

The total volume of the mixtures was kept at 25 ml. All measurements were made at room temperature (25 °C). The order of addition of reactants has no significant effect on absorbance and stability of colour. However, in the present studies, the order of addition of reactants was CAS solution, buffer solution, palladium solution and lastly CTAB or CPB solution.

RESULTS AND DISCUSSION

In Figure 1 absorption spectra of solutions containing CAS (curve A), CAS and Pd^{2+} (curve B), CAS and CTAB (curve C), CAS and CPB (curve D), CAS, Pd^{2+} and CTAB (curve E) and CAS, Pd^{2+} and CPB (curve F) are presented at PH = 5.0 maintained by acetate buffer. The formation of green ternary complexes is exhibited by a bathochromic shift in the absorption maxima to 620 nm and is accompained by a marked increase in absorbance.

The change in absorption characteristics of CAS in the presence of CTAB and CPB at different pH was studied in detail. At pH = 5.0, solutions containing CAS, CAS and CTAB and CAS and CPB show maximum absorption at 430, 420 and 420 nm respectively. Absorption spectra of solutions containing CAS and a 20-fold excess of CTAB and CPB were recorded over the pH range 1.5 to 8.9. Absorption spectra of solutions containing a fixed amount of CAS and different amounts of CTAB and CPB were also recorded at pH 5.0. The absorption maxima shifted to 420 nm for which atleast a 4-fold excess of CTAB or CPB was required.

Absorption spectra of solutions containing Pd^{2+} and CAS in different proportions and varying amounts of CTAB or CPB were recorded at pH 5.0. These spectra indicate the formation of only one ternary complex in each

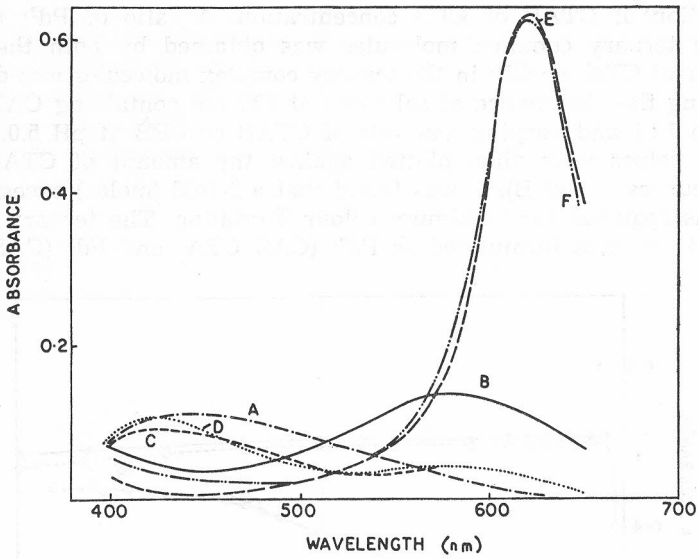


Figure 1. Change in absorption characteristcs of CAS and a binary complex of CAS with palladium ions in the presence of CTAB and CPB. Final concentration of reactants; CAS, 1.2×10^{-5} M; Pd^{2+}, 1.2×10^{-5} M, CTAB, 1.2×10^{-4} M; CPB, 1.2×10^{-4} M; and pH 5.0. A, CAS; B, CAS + Pd^{2+}; C, CAS + CTAB; D, CAS + CPB; E, CAS + Pd^{2+} + CTAB; F, CAS + Pd^{2+} + CPB.

ternary system under the experimental conditions. The absorbance of these solutions at 620 nm were plotted against the amount of CTAB or CPB. From these plots it was concluded that in order to obtain maximum absorbance of green colour, at least a 2-fold excess of CTAB or CPB was required.

The ratio of Pd^{2+} and CAS in the ternary complex molecule was established by Job's method of continuous variations[12,13] and the molar ratio method[14] in the presence of a suitable constant and an excess amount of CTAB or CPB. This constant concentration of CTAB or CPB was adjusted in such a manner that in all the mixtures CTAB or CPB was present in a 2 to 50-fold excess with respect to Pd^{2+} concentration and the absorbance of the mixtures was

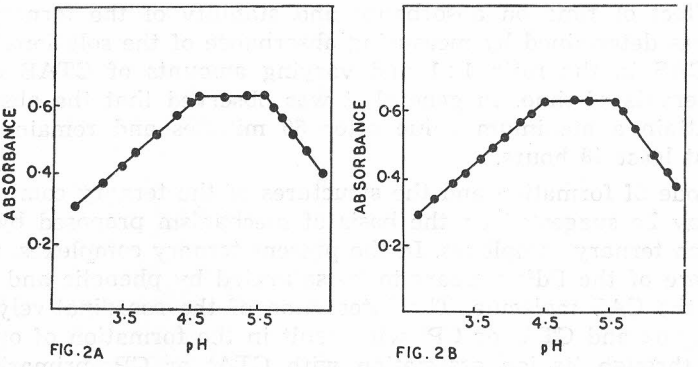


Figure 2. Variation of absorbance with pH of the binary complex of CAS with Pd^{2+} in the presence of CTAB and CPB. Final concentration of reactants; CAS, 1.2×10^{-5} M; Pd^{2+}, 1.2×10^{-5} M; CTAB, 1.2×10^{-4} M; CPB, 1.2×10^{-4} M. A, CAS + Pd^{2+} + CTAB; B, CAS + Pd^{2+} + CPB.

not a function of CTAB or CPB concentration. A ratio of Pd^{2+} to CAS of 1 : 1 in the ternary complex molecules was obtained by both the methods. The number of CTA^+ or CP^+ in the ternary complex molecules was determined by measuring the absorbance of solutions at 620 nm containing CAS and Pd^{2+} in the ratio 1 : 1 and varying amounts of CTAB or CPB at pH 5.0. Measured absorbance values were then plotted against the amount of CTAB or CPB (Figure 3, curves A and B). It was found that a 2-fold (molar) excess of CTAB or CPB was required for maximum colour formation. The ternary complexes investigated are thus formulated as Pd^{2+} (CAS) CTA_2 and Pd^{2+} (CAS) CP_2.

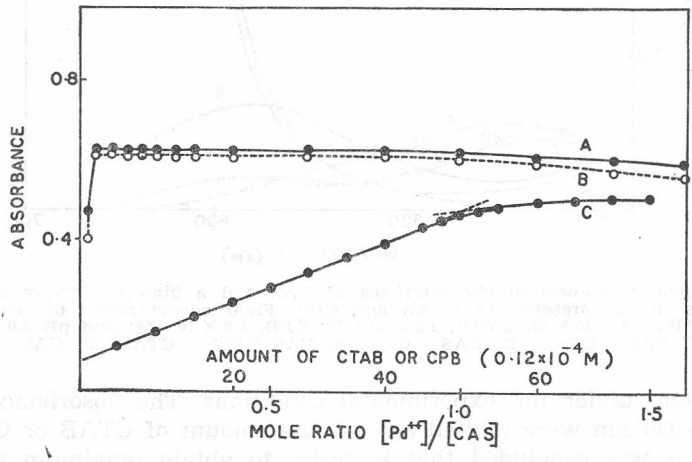
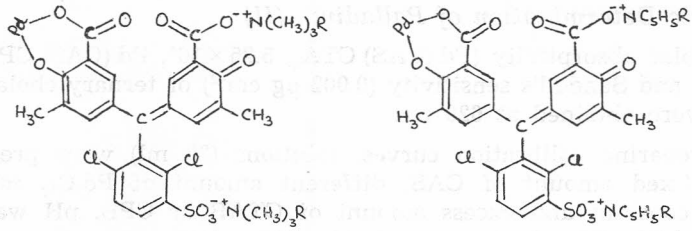


Figure 3. A, Graph of absorbance versus amount of CTAB. B, Graph of absorbance versus amount of CPB. Final concentration of reactants; CAS, 1.2×10^{-5} M; Pd^{2+}, 1.2×10^{-5} M; pH, 5.0; 620 nm. C, Graph of absorbance versus molar ratio Pd^{2+}/CAS Final concentration of CAS, 2.0×10^{-5} M; pH = 5.0 at 580 nm.

In order to obtain the optimum pH range over which λ_{max} and absorbance of the ternary complexes remained unchanged, absorption spectra of solutions containing Pd^{2+}, CAS and CTAB or CPB in the ratio 1 : 1 : 10 at different pH were recorded. The λ_{max} remained unchanged between pH 3.5 to 6.0 but the absorbance was constant only between pH 4.6 to 5.6 (Figure 2A and 2B).

The effect of time on absorbance and stability of the ternary complex solutions was determined by measuring absorbance of the solutions containing Pd^{2+} and CAS in the ratio 1 : 1 and varying amounts of CTAB or CPB at regular intervals of time. In general it was observed that the absorbance of solutions attain a maximum value after 60 minutes and remained constant for up to at least 48 hours.

The mode of formation and the structures of the ternary complexes investigated may be suggested on the basis of mechanism proposed by Bailey et al.[15] for such ternary complexes. In the present ternary complexes, the coordination sphere of the Pd^{2+} appears to be saturated by phenolic and carboxylic oxygen of the CAS molecule. The interaction of the coordinatively saturated binary complex and CTA^+ or CP^+ will result in the formation of outer-sphere complexes through its ion association with CTA^+ or CP^+ primarily via the sulphonic acid group. The ternary complexes investigated may therefore be represented by the following structures:



It was observed above that in the formation of the present ternary complexes we considered only equilibria involving changes in the outer sphere and therefore, the formation of these ternary complexes can be described in a stepwise manner in terms of the following equations (charges have been omitted for simplicity):

$$\mathrm{Pd} + \mathrm{CAS} \overset{K_1}{\rightleftharpoons} \mathrm{Pd\,(CAS)} \tag{1}$$

$$\mathrm{Pd\,(CAS)} + 2\,\mathrm{CP} \overset{K_2}{\rightleftharpoons} \mathrm{Pd\,(CAS)CP_2} \tag{2}$$

K_1 and K_2 can be evaluated separately by the same experimental and calculation methods[16], in the present case by absorbance measurements employing the molar ratio method[14]. K_1, K_2 and β (overall formation constant of the ternary complex) are given by the following expressions:

$$K_1 = \frac{[\mathrm{Pd\,(CAS)}]}{[\mathrm{Pd}]\,[\mathrm{CAS}]} \tag{3}$$

$$K_2 = \frac{[\mathrm{Pd\,(CAS)CP_2}]}{[\mathrm{Pd\,(CAS)}]\,[\mathrm{CP}]^2} \tag{4}$$

$$\beta = K_1 K_2 \tag{5}$$

K_1 and K_2 were calculated by the molar ratio method using absorbance data (Figure 3) employing in following expressions:

$$K_1 = \frac{C_1 (1 - \alpha_1)}{\alpha_1^2 C_1^2} \tag{6}$$

$$K_2 = \frac{C_2 (1 - \alpha_2)}{\alpha_2 C_2 (2\,\alpha_2 C_2)^2} \tag{7}$$

where, α_1 and α_2 are the degree of dissociation of Pd (CAS) and Pd (CAS) CP_2 respectively and C_1 and C_2 are the concentration of CAS and the corrected concentration of Pd (CAS) respectively.

TABLE I

Conditional Formation Constant Values of Ternary Complexes

Ternary complex	C_1	α_1	Log K_1	C_2	α_2	Log K_2	β'(Log $K_1 K_1$)
Pd (CAS) CTA_2	2.0×10^{-5} M	0.078	6.88	0.6×10^{-5} M	0.0158	15.24	22.12
Pd (CAS) CP_2	2.0×10^{-5} M	0.078	6.88	0.6×10^{-5} M	0.0161	15.21	22.09

Photometric Determination of Palladium (II)

The molar absorptivity (Pd (CAS) CTA_2, 5.25×10^4; Pd (CAS) CP_2. 6.16×10^4 mol^{-1} cm^{-1}) and Sandell's sensitivity (0.002 μg cm^{-2}) of ternary chelate forming reactions were obtained at 620 nm.

For preparing calibration curves, solutions (25 ml) were prepared containing a fixed amount of CAS, different amount of $PdCl_2$ solution and a suitable constant and excess amount of CTAB or CPB. pH was adjusted to 5.0 by adding 3.0 ml of acetate buffer. Absorbance was measured after 1 hour at 620 nm and plotted against the amount of palladium. Beer's law range was obeyed over the range 0.053 to 2.98 ppm of palladium. A sample solution containing palladium in this concentration range was treated with equal amounts of CAS and CTAB or CPB. pH was adjusted to 5.0 by acetate buffer. Absorbance was measured at 620 nm and the concentration of palladium was determined directly from calibration curves corresponding to this absorbance value. Ru(III), Zr(IV) and ClO_4^- interfere seriously in the determination and therefore must be removed from the sample solution by suitable methods.

The method was tested in the presence of various cations and anions, and the tolerance limits of the different ions, corresponding to a 2% change in absorbance, are given in Table II. The precision of colour reactions was determined in terms of the mean and relative standard deviations, which were found to be ±0.003 and ±1.5% respectively at 620 nm. The mean relative error (0.5%) in the determination of palladium was obtained at 620 nm.

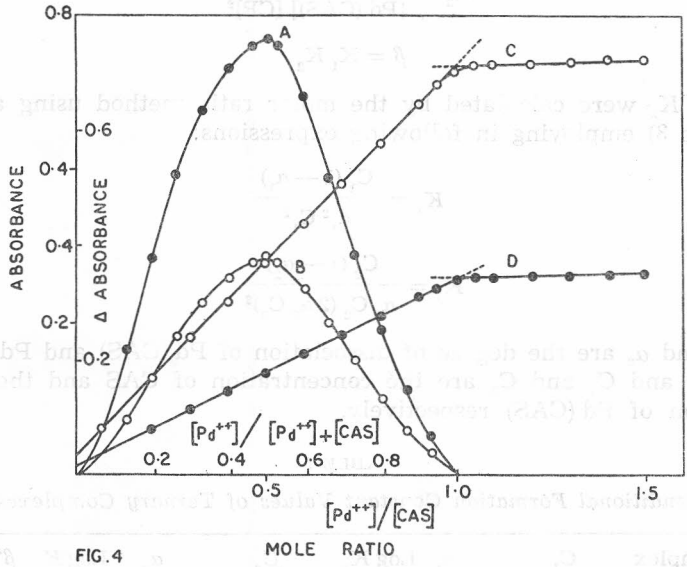


Figure 4. Job's plots: Original concentration of CAS, Pd^{2+} and final concentration of CTAB and CPB; A, CAS (5.0×10^{-5} M); Pd^{2+} (5.0×10^{-5} M); CTAB (3.0×10^{-4} M); B, CAS (2.5×10^{-5} M); Pd^{2+} (2.5×10^{-5} M); CPB (1.5×10^{-4} M); pH 5.0 at 620 nm. Change in absorption characteristics of the binary complex of CAS with Pd^{2+} with a constant amount of CTAB or CPB, molar ratio plots: Final concentration of reactants; C, CAS (1.0×10^{-5} M), CTAB (2.0×10^{-4} M); D, CAS (0.5×10^{-5} M), CPB (1.0×10^{-4} M); pH = 5.0 at 620 nm.

TABLE II

Effect of Cations and Anions on Palladium Determination: Pd^{2+} (1.2×10^{-5} M), CAS (1.2×10^{-5} M), CTAB (2.4×10^{-5} M), CPB (2.4×10^{-5} M), pH 5.0 and *Temperature* 25 °C

Foreign ions	Added as	Tolerance limit corresponding to 2% change in absorbance	
		Pd-CAS-CTAB system	Pd-CAS-CPB system
Hg^{2+}	$HgCl_2$	337	333
Al^{3+}	$AlCl_3$	216	212
Ca^{2+}	$CaCl_2$	321	313
La^{3+}	$LaCl_3$	278	278
Nd^{3+}	$NdCl_3$	289	286
Mg^{2+}	$MgCl_2$	241	237
Pb^{2+}	$Pb(NO_3)_2$	332	324
Zr^{4+}	$ZrOCl_2$	26	25
Ba^{2+}	$BaCl_2$	330	327
UO_2^{2+}	$UO_2(NO_3)_2$	312	302
VO^{2+}	$VOSO_4$	276	267
Ta^{5+}	$TaCl_5$	290	286
$Cr_2O_7^{2-}$	$K_2Cr_2O_7$	250	245
MnO_4^-	$KMnO_4$	220	216
Fe^{2+}	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	268	260
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	254	249
Cd^{2+}	$Cd(NO_2)_2$	279	275
Ru^{3+}	$RuCl_3$	75	72
Rh^{3+}	$RhCl_3$	330	326
OsO_5^{2-}	H_2OsO_5	396	390
Ir^{4+}	$IrCl_4$	400	396
Pt^{4+}	H_2PtCl_6	421	421
ClO_4^-	$NaClO_4$	Precipitated	Precipitated
I^-	KI	2020	2010
CO_3^{2-}	Na_2CO_3	1680	1668
SO_3^{2-}	Na_2SO_3	2562	2562
PO_4^{3-}	Na_2HPO_4	2279	2241
CH_3COO^-	CH_3COONa	2309	2300
Cl^-	NaCl	7100	7080
NO_3^-	$NaNO_3$	7440	7416

Conclusion

The proposed spectrophotometric method, involving ternary complexes of palladium with CAS and CTAB or CPB, for the microdetermination of palladium is precise, sensitive and selective. The ions which interfere seriously in the determination of palladium are Ru(III), Zr(IV) and ClO_4^-. For establishing palladium and CAS ratios in the ternary complexes by Job's method of continuous variations and by the mole ratio method and for determining Beer's Law range, it is essential to adjust the CTAB or CPB concentration

carefully in such a manner that the absorbance of the mixture is not a function of CTAB or CPB concentration. A simple method is suggested for the evaluation of the conditional formation constant values of the ternary complexes, especially applicable in the case of outer-sphere ternary complexes. The mode of formation and structure of ternary complexes are discussed on the basis of the mechanism proposed by Bailey et al.

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SAŽETAK

Miješani kompleksi paladija s chromeazurol S i cetiltrimetilamonij-bromidom odnosno cetilpiridinium-bromidom

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Ispitano je nastajanje miješanih, zeleno obojenih, kompleksa paladija s chromeazurol S i cetiltrimetilamonij-bromidom odnosno cetilpiridinium-bromidom u području pH od 4,6 do 5,6. Sastav kompleksa određen je spektrofotometrijski Job-ovom metodom kontinuiranih varijacija i metodom molnih udjela. Uz sadržaj paladija od 0,053 do 2,98 ppm sistem slijedi Beer-ov zakon. Kod 620 nm molarni apsorpcijski koeficijenti iznose $5{,}25 \cdot 10^4$ odnosno $5{,}16 \cdot 10^4$ mol^{-1} cm^{-1} i Sandell-ova osjetljivost 0,002 μg cm^{-2}.

Predloženo je korištenje ovih miješanih kompleksa za spektrofotometrijsko određivanje paladija i ispitan je utjecaj niza kationa i aniona. Diskutirana je i struktura kompleksa.

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