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Extraction of Palladium-[4-(2-Thiazolylazo)Resorcinol] Complexes and Spectrophotometric Determination of Palladium

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The extraction of palladium(II) as a red comples with 4-(2--thiazolylazo)resorcinol (TAR = H_2R) by tetraphenylphosphonium chloride in chloroform was studied. Quantitative extraction was achieved in the pH region between 2 and 10. By extraction at pH 2 and by spectrophotometric measurements of the red complex in the organic phase, a sensitive and selective method for palladium determination was evaluated. An anionic complex $[PdRCl]^-$ was predominantly extracted over a wide pH range forming ion associates with tetraphenylphosphonium cation ($\lambda_{max} = 525$ nm, $\varepsilon = 2.4 \times 10^4$ 1 mol^{-1} cm^{-1}). The extracted complexes were studied in solution and by characterization of the isolated solid compounds.

INTRODUCTION

Palladium(II) reacts with 4-(2-thiazolylazo)resorcinol (TAR) forming green and red coloured complexes, depending on pH[1-3]. In aqueous solution, colloidal turbidity or a precipitate gradually appears, making the system unsuitable for spectrophotometric analysis.

Mixed aqueous dimethylformamide solution remained clear and was proposed for the spectrophotometric determination of palladium in 1.0—1.5 M $HClO_4$ (green complex) and at pH 5.0—5.5 (red complex). Complexation equilibria in this homogeneous mixed medium were studied in detail[1]. The reaction of palladium and TAR in the presence of cation-active tensides resulted in the formation of a soluble ternary complex with small bathochromic shifts in the absorbance maximum[2]. The green palladium-TAR complex formed in sulphuric acid solution could be extracted into isoamyl alcohol and measured spectrophotometrically in the organic phase[3]. The determination of palladium based on the green complex[1,3] was selective, but less sensitive than that based on the use of red complexes at pH 5[1,2].

The present work deals with the extraction of palladium-TAR complexes by tetraphenylphosphonium chloride, with the study of the extracted species and their use for the spectrophotometric determination of palladium. By comparison with the extraction behaviour of palladium 4-(2-pyridylazo)resorcinol (PAR) complexes[4], differences and similarities of PAR and TAR reagents are demonstrated.

EXPERIMENTAL

Aparatus

Visible region spectra and absorbance measurements were made with a Perkin-Elmer Coleman 124 spectrophotometer. Infrared spectra of the isolated compiexes were recorder on Perkin-Elmer spectrophotometers Models 257 (4000—600 cm^{-1}) and 508B (4000—200 cm^{-1}). Palladium derminations by atomic — absorption spectrometry were performed with a Perkin-Elmer 5000 AA spectrometer, and by atomic emission spectrometry with an ARL 35000 C-ICP plasma spectrometer. The pH of the aqueous phase was measured with a Radiometer M 64 pH meter. A Griffin Flask Shaker with a stop watch was used for the extraction.

Reagents

All the chemicals used were analytical grade reagents. 4-(2-Thiazolylazo)resorcinol and tetraphenylphosphonium chloride were from Fluka (Buchs, Switzerland). Their purity was verified by elemental analysis. Deionized-distilled water was always used.

Standard Solution of Palladium

A stock solution of palladium chloride (1×10^{-2} M) was prepared by dissolving 0.45 g of $PdCl_2$ in 250 ml HCl (0.1 M). The solution was standardized by gravimetric determination of palladium with dimethylglyoxime[5].

A stock solution of 4-(2-thiazolylazo)resorcinol (1×10^{-2} M) was prepared by dissolving a weighted amount of substance (0.1106 g) in 5 ml of 1 M NaOH followed by dilution with deionized-distilled water to 50 ml in a volumetric flask. Solutions of lower concentration were prepared by dilution daily.

Extraction Procedure

Aqueous solutions (10 ml) containing palladium (II) (5×10^{-6} to 8×10^{-5} M), TAR ($5 \times 10^{-6} - 4 \times 10^{-4}$ M), chloride ($1 \times 10^{-3} - 5 \times 10^{-1}$ M) and buffer were extracted (within 5—60 minutes after mixing the reactants) with 10 ml of chloroform containing tetraphenylphosphonium chloride ($1 \times 10^{-4} - 1 \times 10^{-2}$ M) by shaking for 10 min on a mechanical shaker. After equilibration and separation of the layers, 5 ml of either phase was taken for the determination of palladium by atomic absorpion spectrometry. (In the aqueous phase palladium was determined directly, and in the organe phase after chloroform evaporation and dissolution of the residue in 5 ml of ethanol). An aliquot of the chloroform phase was used for parallel spectrophometric measurement of the palladium-TAR complex at 525 nm.

Recommended Procedure for Palladium Determination

Into a 50-ml conical flask pipette a slightly acidic aqueous solution of palladium (5 ml) containing 1—50 μg of palladium. Add 2 ml of 1×10^{-3} M TAR and 3 ml of citrate buffer pH 2 containing 0.06 M chloride. Extract once with 10 ml 1×10^{-3} M tetraphenylphosphonium chloride in chloroform, shaking for 10 min on a mechanical shaker. Separate the phases and measure the absorbance of the organic phase at 525 nm in 1-cm cells against the extract of reagent blank.

Composition of the Extracted Complexes

The molar ratio of palladium to TAR and the tetraphenylphosphonium to Pd-TAR species in the extracted complex was determined spectrophotometrically by Job's and slope-ratio methods.

Preparation of Solid Complexes

To 100 ml of 1×10^{-2} M TAR in 0.2 M NaOH 500 ml of 2×10^{-3} M $PdCl_2$ in 0.04 M HCl was added slowly, with stirring. The pH of the reaction mixture

was checked by pH-meter and adjusted to 2 or 6 (with HCl, and NaOH). The reaction mixture was then transferred to a separatory funnel and extracted with 150 ml of chloroform containing the equivalent amount of Ph_4PCl (1 mmol, 374 mg). The chloroform phase was separated and its volume was reduced to 50 ml. Ethyl acetate (50 ml) was added and left to stand for 24 hours in a refrigerator. Subsequently petroleum ether (50 ml) was added and the mixture was left to stand for about 3 hours. The red crystals were filtered off, washed with petroleum ether and dried in a vacuum desiccator over silica gel. The yield was about 40%.

Elemental Analysis

Palladium in the isolated complexes was determined gravimetrically with dimethylglyoxime[5] and also by the ICP-AES method, after decomposition of the substance (10 mg) by the Kjeldahl method.

Chloride was determined by indirect EDTA titration, after decomposition of the substance by the oxygen-flask combustion method, precipitation of chloride as silver chloride, and its dissolution in tetracyanonickelate.[6] Carbon, hydrogen, nitrogen and sulphur were determined by the usual microanalytical methods. Phosphorus was determined by the ICP-AES method[7].

The analytical data were consistent with the formula $[Ph_4P]$ [PdRCl] $C_{33}H_{25}N_3O_2SPClPd$ (M_r = 700.43).

Calc.:	C 56.58, H 3.89, N 6.00, S 4.58, P 4.42, Cl 5.06, Pd 15.19%.
Found (A):	C 56.31, H 3.88, N 6.10, S 4.80, P 3.81, Cl 4.96, Pd 15.06%.
Found (B):	C 56.70, H 3.89, N 6.16, S 4.83, P 3.85, Cl 5.18, Pd 15.25%.

A and B denote complexes extracted from aqueous solution at pH 2 and 6, respectively.

RESULTS AND DISCUSSION

4-(2-Thiazolylazo)resorcinol (TAR) like 4-(2-pyridylazo)resorcinol (PAR) forms green and red coloured complexes with palladium(II). The green complexes are extractable in some polar solvents. The red complexes can be extracted in chloroform and similar solvents by addition of tetraphenylarsonium and tetraphenylphosphonium chloride. Most experiments in this work were performed with tetraphenylphosphonium chloride wich was more readily available. The distribution of palladium between the aqueous and chloroform phases was followed by atomic-absorption spectrometry (AAS) and by absorbance measurements of the palladium-TAR complex in the organic phase.

The red palladium complexes with PAR and TAR were efficiently extracted over a wide pH range. The absorbance — pH curve for TAR complexes was shifted to a more acidic region showing practically identical absorbance values at 525 nm in the pH range 2 — 10 (Figure 1, curve 1). Under the same conditions palladium-PAR complexes are quantitatively extracted above p*H* 3[4]. The shift to a lower pH value indicates that the *p*-hydroxy group of TAR coordinated to palladium is ionized at a lower pH value than that of coordinated PAR[8]. This is in agreement with the earlier findings that TAR complexes are generally more acidic than those of PAR[9].

Extraction of palladium-TAR complexes from the aqueous phase with a lower pH than the optimum for their direct spectrophotometric measurements in the aqueous or homogeneous mixed media[1,2] was advantageous. Selectivity was much improved, owing to a more selective reaction of TAR at lower pH. Reproducibility and realiability of analytical results were also

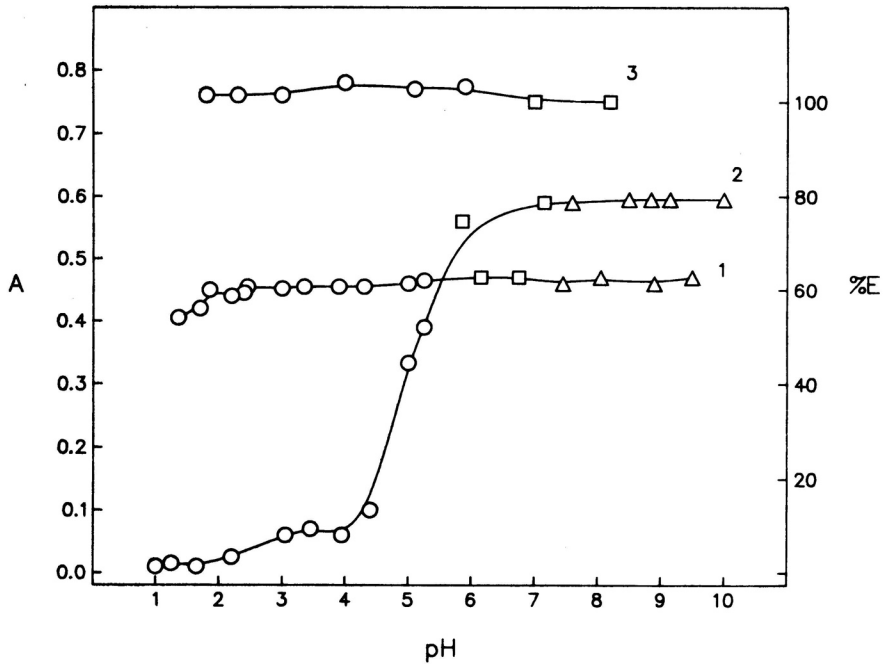

Figure 1. Dependence of extraction on pH

Curves 1 and 2, absorbance of organic phase at 525 nm (left-hand ordinate)
1, c (Pd) = c (TAR) = 4×10^{-5} M, c (Ph_4PCl) = 1×10^{-3} M
2, c (TAR) = 4×10^{-5} M, c (Ph_4PCl) = 1×10^{-3} M
Curve 3, per cent extraction of palladium obtained by AAS-data (right-hand ordinate)
c (Pd) = 2×10^{-5} M ; c (TAR) = 2×10^{-4} M ; c (Ph_4PCl) = 1×10^{-3} M
Buffer solutions: ○ citrate, □ acetate, △ universal

improved owing to a much lower and more constant absorbance value of the reagent blank. Above pH 4, the absorbance of TAR reagent strongly increased (Figure 1, curve 2) as a consequence of the preferred extraction of HR^- species with maximum absorption in the chloroform phase at 470 nm, closer to the absorption maximum of the extracted palladium complex (525 nm) than that of the undissociated H_2R molecule (410—440 nm). In comparison with the method based on measurements of the green complex ($\varepsilon = 8.3 \times 10^3$)[3], the determination of palladium with TAR based on measurements of the red complex was more sensitive ($\varepsilon = 2.4 \times 10^4$) and much less affected by chloride ions, commonly present in the analytical system.

Studies of Extraction and Spectrophotometric Determination at pH 2

Practically complete extraction of palladium was achieved from the dilute solution of palladium chloride with the ligand and extractant in proper excess, and chloride in the concentration range 0.001 — 0.05 M. The optimum excess of the ligand was 5—10-fold and of the extractant above 100-fold over palladium. The extraction equilibria were attained in less than 5 mi-

nutes of shaking. Extraction was carried out within 5 — 60 minutes after mixing the reactants. The absorbance of the organic phase was stable for at least two days. Beer's law was obeyed all over the range of concentrations used (5×10^{-6} — 8×10^{-5} M Pd).

The effect of foreign ions on the extraction and determination of palladium in the organic phase was studied. The ions tested did not interfere up to molar ratios given in Table I. An error of ± 5% in the reading was considered tolerable. A much better selectivity was obtained than with the method based on direct spectrophotometric measurements of the red palladium-TAR complex in homogeneous mixed aqueous medium.[1] Chloride ions in concentrations above 0.05 M decrease the absorbance of the organic phase, but much less than that of the palladium-PAR complex extracted at pH 6[4].

TABLE I

Tolerance to foreign ions in the determination of palladium by the recommended procedure

c (Pd) = 4×10^{-5} M, c (TAR) = 2×10^{-4} M, c (Ph_4PCl) = 1×10^{-3} M

Ion	Tolerance Molar ratio Ion:Pd
Acetate, citrate, sulphate, phosphate, tartarate	10000:1
Oxalate, Mn (II), Ca (II), Mg (II), Al (III), Ni (II), Zn (II), Cd (II)	1000:1
Nitrate, Cu (II), Co (II), Nb (V), U (VI), EDTA[a], DCTA[a]	100:1
Cyanide, fluoride[a] Pb (II), Ti (IV)	10:1
Zr (IV), Bi (III)	5:1

[a] Maximum ratio tested

Composition of the Extracted Complexes

The composition of the extracted complexes was determined spectrometrically by means of Job's and the slope-ratio methods (Figures 2 and 3). The molar ratio of the tetraphenylphosphonium to palladium to TAR in the extracted species was 1 : 1 : 1. Considering the e.quilibria in the palladium--TAR system, different red coloured complex species may be expected in the slightly acidic aqueous phase[1]. The results show that, similarly to the palladium-PAR system, only one anionic mixed ligand species $[PdRCl]^-$ was efficiently extracted, forming ion associates with the tetraphenylphosphonium cation. It had the absorption maximum at 525 nm with molar absorpitivity 2.4×10^4 1 mol^{-1} cm^{-1}. The same species was extracted throughout the pH range 1—10, even though the dominant species in the aqueous phase were changed by altering the pH.

As it was already realized in the study of extraction of palladium-PAR complexes, solution studies alone cannot confirm that chloride has taken

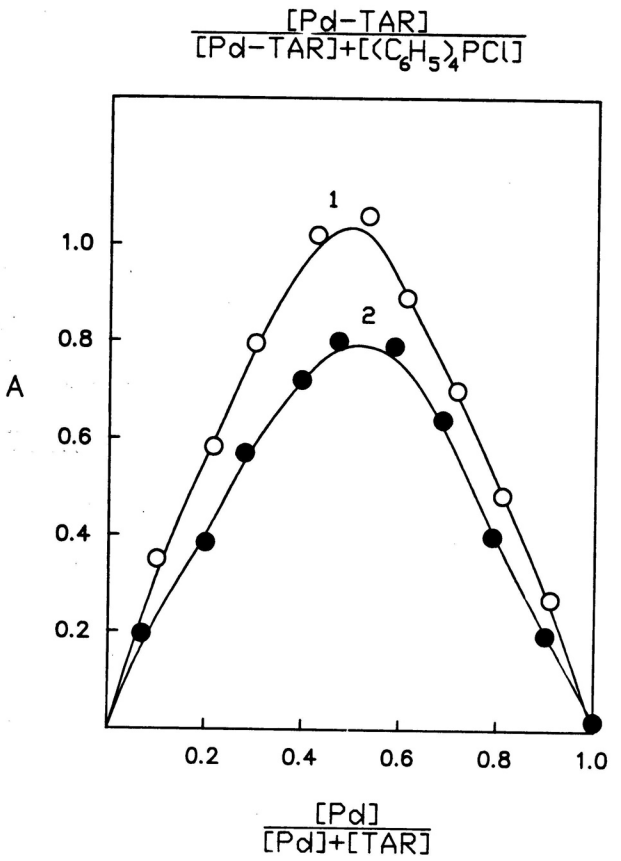

Figure 2. Composition of the complex extraced at pH 2, determined by Job's method

Curve 1, Palladium to TAR ratio (lower abscissa)
c (Pd) + c (TAR) = 1×10^{-4} M ; c (Ph_4PCl) = 1×10^{-3} M
Curve 2, Extractant to palladium-TAR complex ratio (upper abscissa)
c (Pd-TAR) + c (PH_4PCl) = 1×10^{-4} M

part in the formation of the extracted species. Therefore, we separated the extracted complexes and characterized them in the solid state. The complexes isolated from the organic phase obtained by extraction at pH 2 and 6 were identical, which was verified by elemental analysis and by comparison of infrared and visible spectra. The analytical data were consistent with the formula [Ph_4P][PdRCl], where R denotes a divalent anion of TAR ligand (H_2R).

The infrared spectra of the isolated complexes show absorption bands characteristic of tridentately coordinated TAR: a strong band at 1580 comprising C = C, C = N and C = O stretching modes, a very strong band at 1375 cm^{-1}, which is related to the stretching of the azo group coordinated through the single nitrogen atom, and a few bands in the region 1320—1140

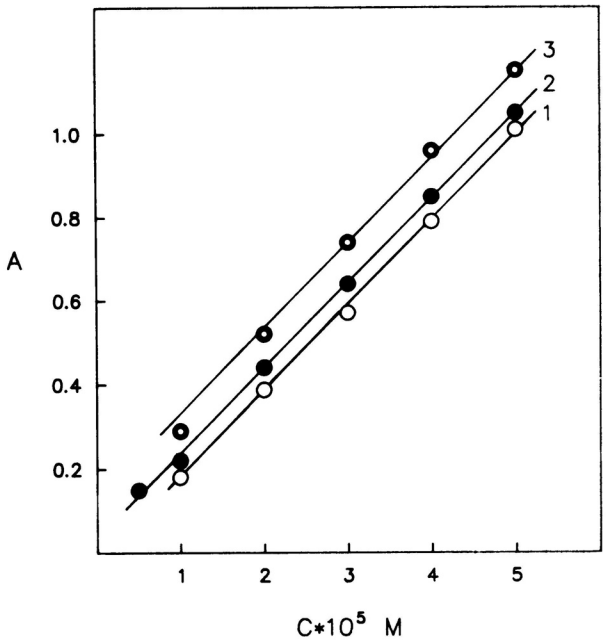

Figure 3. Composition of the extracted complex determined by the slope-ration method

Curve 1, c (Pd-TAR) = 2×10^{-4} M ; c (Ph_4PCl) varied
Curve 2, c (Pd) = 2×10^{-4} M ; c (Ph_4PCl) = 1×10^{-3} M , TAR varied
Curve 3, c (TAR) = 1×10^{-4} M ; c (Ph_4PCl) = 1×10^{-3} M ; c (Pd) varied

originating in various C—C, C—N, C—O and C—H stretching and deformation modes[10,11]. From the spectral evidence it could be assumed that PAR and TAR coordinate to palladium in the same way as to other metals, i.e. through one nitrogen of the azo group, the phenyl oxygen on the ortho-position and throught the nitrogen of the heterocyclic ring, as it was verified by crystal structure analysis of vanadium complexes[12,13]. The chloride ion present in the extracted complex most probably enters the coordination sphere of palladium, which would then achieve a coordination number of four.

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SAŽETAK

Ekstrakcija paladijevih kompleksa sa 4-(2-tiazolilazo)rezorcinolom i spektrofotometrijsko određivanje paladija

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Proučavana je ekstrakcija paladija u obliku crvenih kompleksa sa 4-(2-tiazolilazo)rezorcinolom (TAR = H_2R). S pomoću tetrafenilfosfonij-klorida paladij se kvantitativno ekstrahira u kloroform u području $2 < pH < 10$. Razrađena je osjetljiva i selektivna metoda za određivanje paladija, koja se temelji na ekstrakciji crvenog kompleksa pri $pH = 2$ i mjerenju apsorbancije organske faze ($\lambda_{max} = 525$ nm, $\varepsilon = 2,4 \times 10^4$ L mol^{-1} cm^{-1}). Određivanjem sastava kompleksa u otopini i karakteriziranjem kompleksnih spojeva izoliranih iz organske faze utvrđeno je da se u širom pH-području pretežno ekstrahira anionski kompleks $[PdRCl]^-$ kao ionski asocijat s tetrafenifosfonij kationom.