SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM (II)

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Chlorpromazine tetrabromopalladium (II), promethazine tetrabromopalladium (II), chlorpromazine tetraiodo palladium (II) and promethazine tetraiodopalladium (II) were prepared and characterized by IR, VIS spectra and elemental analysis. A sensitive, inexpensive and rapid spectrophotometric method for the determination of palladium (II) has been elaborated. The method allows determination of palladium (II) has been elaborated. The method allows determination of palladium (II) in the range of 10-100 µg m⁻¹. It was checked by the determination of palladium (II) in Degussa's catalyst (E-207 R).

Key words: Palladium (II), Chlorpromazine palladium (II) complexes, Promethazine-Palladium (II) complexes, Spectrophotometry.

Introduction

The development of fast, sensitive and efficient methods for the determination of palladium (II) is important for use in analytical chemistry and environmental protection due to the wide usage of palladium in catalysis Palladium (II) can be determined by means of electroanalytical or spectroanalytical methods. Among the latter methods spectrophotometery is wide used but it seems interesting to improve the methods with new organic reagents (Marczenko 1968) During to Pd (II) inertness and soft acid character, ligands with sulphur donor atoms are used as organic reagents (Sikorska-Tomicka and Czerepko 1983). Pd (II) forms negatively changed anionic complexes with halides (Cl⁻, Br⁻, I⁻). Anionic Pd(II) halide complexes with phenothiazine derivatives produce stable ionic pairs which can be quantitatively extracted with chloroform (Dembinski 1983).

The aim of the present paper is to prepare palladium (II)complexes with chlorpromazine: [2-chloro-10-(3-dimethylaminopropyl) phenothiazine] and promethazine: [12-dimethylaminopropyl) phenothiazine] in the form of hydrochlorides which can be used for a new complexing reagents (Paweczyk 1986). Since the obtained compounds were intensively coloured and stable, can be applied in spectrophotometric method for determination of Pd (II) trace amounts. The new Pd(II) complexes will be characterized by IR and UV-VIS spectra. The elaborated method of Pd (II) determination by the use of phenothiazine derivatives is convenient for Pd (II) analysis and can also be inverted for the determination of these organic compounds.

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Experimental

Reagents. Palladium chloride-aqueous solutions 1.00×10^{-2} mol.dm⁻³ and 1.2×10^{-4} mol-dim⁻³· Chlorpromazine hydrochloride aqueous solutions 1.00×10^{-1} mol-dm⁻³ and 1.06×10^{-4} mol. dm⁻³; Promethazine hydrochloride-aqueous solutions 1.00×10^{-1} mol.dm⁻³ and 1.11×10^{-4} mol.dm⁻³. Degussa's catalyst. (E-207R)-Pd 10%/carbons active. Standard Pd(II) solutions were determined using the spectrophotometric method (Morrow and Markham 1964). Chlorpromazine hydrochloride (98%) and promethazine hydrochloride ((98%) were purchased from Aldrich and used without purification. Concentration of phenothiazine derivative solutions was determined using the spectrophotometric method (Dembinski 1977). All used chemicals were analytical grade purchased from POCH Gliwice.

Apparatus. IR spectra were obtained with Spectrum 2000 FT Perkin-Elmer IR spectrophotometer in the range 4000-50 cm⁻¹ using KBr discs. Absorption UV-VIS (28000-15000 cm⁻¹) spectra in chloroform solutions were measured with a M40 Carl Zeiss Jena spectrophotometer.

Preparation of Pd(II) complexes. To 50 ml (0.01 mol. dm⁻³) aqueous solution of palladium (II) chloride, 5 ml H₂SO₄ (2 mol.dm⁻³) and 15 ml of potassium iodide (1 mol.dm₋₃) aqueous solution were added. Bromide Pd(II) complex was prepared similarly. Next 20 ml of hydrochloride chlorpromazine (0.1 mol.dm⁻³ water solution) was added in small portions to the prepared solution and intensively mixed. As the result of the reactions between the anionic iodied (bromide) Pd(II) complexes and chlorpromazine a brown precipitate of chlorpromazine tetraiodopalladium (II) and violet precipitate of chlorpromazine tetrabromopalladium (II) were

obtained. The obtained complexes were filtered, washed with water and recrystallized from ethanol.

Promethazine tetraiodopalladium (II) and promethazine tetrabromopalladium (II) were prepared simlarly. Stoichiometric composition of the compounds was confirmed based on elemental analyses results: (%) (calc./found) (1) $(C_{17}H_{20}N_2S.H)_2.[PdI_4]$, Pd (8.98/8.72), C (34.47/33.98), H (3.51/3.21), N (4,73/4.29); (2) $(C_{17}N_{20}S_2.H)_2 [PdBr_4]$, Pd (10.68/10.33), C (40.96/40.56), H (4.25/4.07), N (5.62/5.39); (3) $C_{17}H_{19}N_2ClS.H)_2.[PdI_4]$, Pd (8.49/8.22), C (32.57/32.18), H (3.22/2.96), N (4.47/4.08); (4) $C_{17}H_{19}N_2ClS.H)_2.[PdBr_4]$, Pd(9.99/9.67), C (38.32/37.91), H (3.78/3.42), N (5.26/4.96).

Results and Discussion

Spectral characteristic. Infrared spectra were analyzed to establish the character of interactions between components of the obtained species. Because of a similar spectral character of the iodide and the bromide complexes with phenothiazine derivatives, only the spectra for chlorpromazine tetrabromopalladium (II) and chlorpromazine tetraiodopalladium (II) are presented in Figure 1. Absorption and in the range 2400-2650 cm^{-1} is characteristic for the amine group vibration in chlorpromazine hydrochloride. The NH band in comparison to phenothiazine derivatives is shifted towards lower were numbers and its intensity has decreased (Bellamy
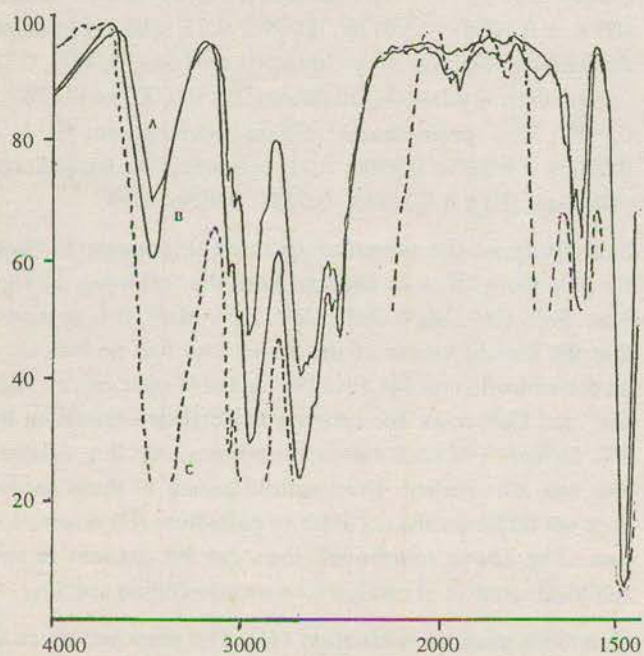
A. chlorpromazine tetrabromopalladium (II); B. chlorpromazine tetraiodopalladium (II); C. chlorpromazine hydrochloride.

Fig 1 IR spectra:
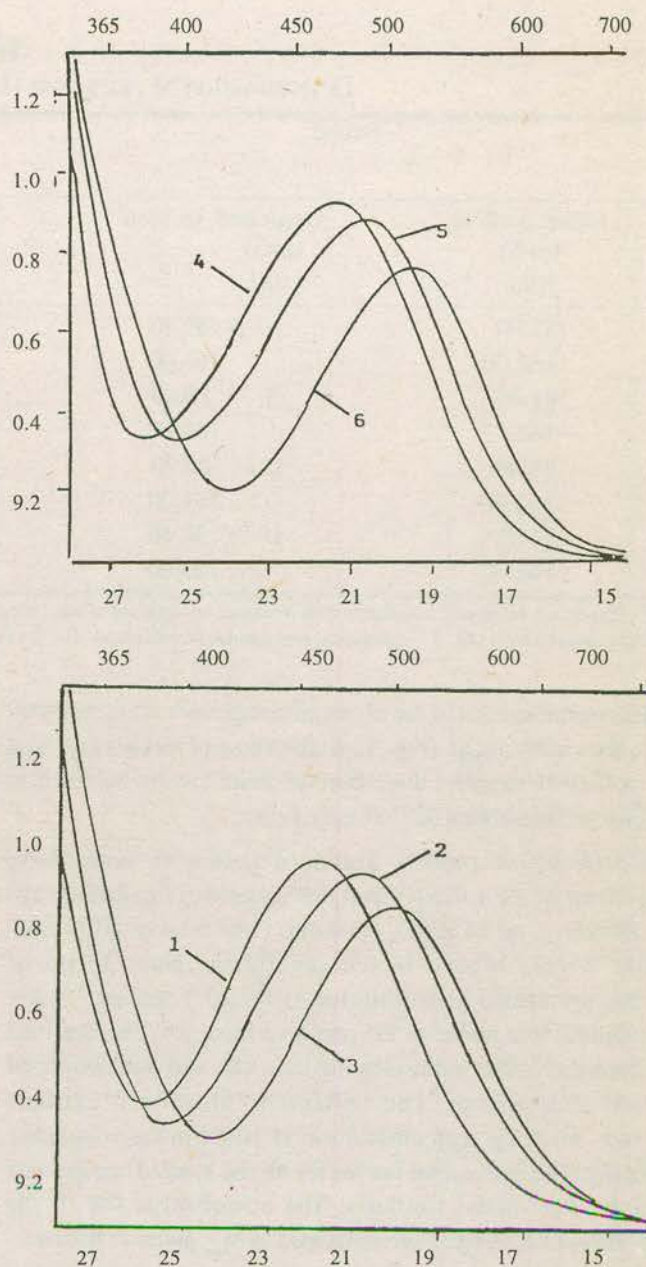
1.chlorpromazine tetraiodopalladium (II); 2. chlorpromazine tetrabromopalladium (II); 3. chlorpromazine tetrachloropalladium (II); 4. promethazine tetraiodopalladium (II); 5. promethazine tetrabomopalladium (II); 6. promethazine tetrachloropalladium (II).

Fig 2. Absorption spectra:

1966). It can be proposed that hydrogen bonds of the crystal lattice, reduce the N-H bond strength causing the above mentioned band shift (Nakamoto 1966). The intensive band at 1706 cm^{-1}, characteristic of amine hydrochlorides (Kross 1951), is absent in the studied spectra. the lack of the band at 1706 cm^{-1} suggests that complexes were formed and chloride ion in hydrochloride chlorpromazine was replaced by the larger $[PdI_4]^{2-}$ or $[PdBr_4]^{2-}$ ions.

Table 1
Determination of palladium (II) in Degussa's catalyst (E-207 R)

Found		Percentage error*)	Standard deviation of the mean	Confidence interval
Iodide method (n=5) [μg]	Described method (n=5) [μg]	[%]	$\overline{S}$ [μg]	$u_{95} = \overline{x} \pm {}_{.195}\overline{S}$ [μg]
81.00	A**) 80.70	-0.37	0.261	80.70±0.726
162.00	• 163.00	0.61	1.560	163.00±4.331
81.00	B. 80.40	-0.75	0.141	80.40±0.392
162	160.00	-1.25	2.010	160.00±5.580
81.00	C. 80.70	-0.37	0.132	80.70±0.367
162.00	161.00	-0.62	1.630	161.00±4.525
81.00	D 80.40	-0.75	0.130	80.40±0.361
162.00	160.00	-1.25	1.400	160.00±3.886

*) Percentage error was calculated with reference to obtained results using the iodied method; **) Palladium (II) was determined as: A - chlorpromazine tetraiodopalladium (II), B - chlorpromazine tetrabromopalladium (II), C - Promethazine tetraiodopalladium (II), D - promethazine tetrabromopalladium III).

Electronic spectra of the obtained compounds were recorded in the visible range (Fig. 2). Large value of molar extinction coefficient suggests that observed band can be assigned to Charge Transitions (CT) (Lever 1984).

Calibration curve. Standard solutions containing 1-10 ml of the 1.02×10^{-4} mol.dm^{-3} solution of palladium (II) chloride, 1 ml of H_2SO_4 (mol.dm^{-3}) and 5 ml of KI (1 mol. dm^{-3}) were placed in ten separators. Next 30 ml of chlorpromazine hydrochloride (1.06×10^{-4}) mol.dm^{-3} water solution) was added to the prepared mixtures. The obtained chlorpromazine tetraiodopalladium (II) salt was extracted with chloroform. The collected chloroform extracts were made up with chloroform to 10 ml in the volumetric flasks. The calibration curves for all the studied compounds were determined similarly. The absorbances for all the obtained couplings were measured at λ_{max} given as follows:

Chloropromazine tetraiodopalladium (II), -465.5 nm; chlorpromazine tetrabromopalladium (II), -478.9 nm; chlorpromazine tetrachloro-palladium (II), -515.5 nm; promethazine tetraiodopalladium (II), -467.6 nm; promethazine tetrabromopalladium (II), 483.6 nm; promethazine tetrachloropalladium (II), -514.4 nm.

The linear dependence of the absorbance on the palladium (II) chloride concentration in the range of 10-100 μg ml^{-1} was established. The calculated molar absorptivities are given as under:

Chloropromazine tetraodopalladium (II), -9.0×10^3 mol^{-1}. dm^3. cm^{-1}; chlorpromazine tetrabromopalladium (II), -8.2×10^3 mol^{-1}. dm^3. chlorpromazine tetrabromopalladium (II), -8.2×10^3 mol^{-1}. dm^3. cm^{-1}; promethazine tetraio-dopalladium (II),

-9.0×10^3 mol^{-1}. dm^3. cm^{-1}; promethazine tetrabromopalladium (II), 8.6×10^3 mol^{-1}.dm^3.cm^{-1}. promethazine tetrabromopalladium (II), 7.6×10^3 mol^{-1}.dm^3.cm^{-1}. The data is elaborated using linear least square. method (equation; correlation coefficient, R; standard deviation, S):

- Chloropromazine tetraiodopalladium (II) y = 0.1077x + 0.0404; 0.9962: 0.22 -chlorpromazine tetrabromopalladium (II) y = 0.1068x - 0.0126; 0.9998; 0.21 -chlorpromazine tetrachloropalladium (II) y = 0.0066x + 0.2581; 0.9993; 0.22 - promethazine tetraiodopalladium (II) y = 0.0093x + 0.1871; 0.9988; 0.31 -promethazine tetrabromopalladium (II) y = 0.0063x + 0.2208; 0.9998; 0.31 -promethazine tetrachloropalladium (II) y = 0.0068x -0.0231; 0.9996; 0.29.

Selectivity of the prepared spectrophotometric method for palladium (II) was checked with the following foreign ions: Sn^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}. It was shown that the tenfold excess of the above ions had no influence on determination results. Fivefold excess of such ions as: Ag^+, Cu^{2+} and Co^{2+} cause the increase in Pd(II)determination by 3%. Influence of such anions as: nitrates, acetates, carbonates was also studied. Even tenfold excess of these anions does not influence the accuracy of palladium (II) determination. The above mentioned ions can be present in the analyzed samples of catalyst as a trace pollution species.

Determination of palladium (II). The proposed spectrophotometric method for determination of palladium (II), was tested on Degussa's catalyst (E-207R), with the declared Pd level at 10%. The results of the determinations of palladium(II) in the catalyst with: chlorpromazine tetraiodopalladium (II), chlorpromazine tetrabromo-palladium (II), promet...

tetraiodopalladium (II) and promethazine tetrabromopalladium (II) are listed in Table 1.

Good convergence between the iodide method (Marczenko 1968) and the proposed spectrophotometric method was found. There are no statistically significant differences in accuracy of determination between the results obtained by these methods.

Conclusions

It was shown that phenothiazine derivatives: (chlorpromazine hydrochloride and promethazine hydrochloride) react with halide complexes of palladium (II) in acid medium, forming intensively coloured compounds.

It has been proved that these compounds are ionic pair salts of protonated chlorpromazine and promethazine with $[PdI_4]^{2-}$, $[PdBr_4]^{2-}$ (L:M=2:1).

The obtained compounds can be quantitatively extracted with chloroform . Taking into account a large stability of the complex in chloroform extract and its high absorption coefficient, the iodide complexes as well as the bromide complexes are convenient for spectrophotometric determination of palladium (II) within the concentration range of 10-100 μg ml^{-1}. Similar results were obtained with bromide complexes.

The elaborated method has the virtue of a suitable selectivity for determination of palladium (II), is quick, simple and inexpensive in realization.

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