

EXPERIMENTAL RESEARCH ON DIVALENT PALLADIUM SPECTRAL DOSING POSSIBILITIES WITH ASYMMETRIC DIOXIMES

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ABSTRACT

Synthesis and use of asymmetric alpha-dioxime in chemical analysis offers chemists the possibility of increasing sensitivity and selectivity colour and precipitation reactions of some transition metals, which is why spectrometric methods for their determination as dioximes have been developed.

In the present work there are shown spectrometric methods for determination of palladium with aliphatic asymmetric dioximes, namely the methyl-ethyl-dioxime, respectively methyl-isopropyl-dioxime are proposed. The asymmetric dioximes are potential organic reagents in the analytic determinations of palladium, as they are extremely sensitive and selective for such metals.

Keywords: aliphatic asymmetric dioximes, palladium, spectrometric methods.

INTRODUCTION

Preparative organic chemistry provides an increasing number of mono- and polycarbonyl combinations for the synthesis of different types. From the numerous oximes mentioned in the specialized literature, only approximately 150 - 200 were studied from coordinative and analytic chemistry point of view. Lately, a series of works has appeared, concerning the study of chemical properties of glucides with azomethinic groups (oximes, thiosemicarbazones), in order to identify the role of heavy metals in the biochemical processes in live bodies [1].

Vicinal dioximes appear in three syn-, amphi- and anti- isomeric forms, depending on the respective position of the functional groups. These geometric isomers were first discovered by Hantzsch and Werner, in the case of benzyl-dioximes [2]. The appearance of the three isomeric forms is characteristic especially for aromatic and heterocyclic dioximes. In the case of aliphatic and alicyclic dioximes, only the anti (α) form was in most cases brought into evidence. For the alicyclic dioximes, the syn (β) and amphi (γ) forms cannot even exist because of sterical hindrance. The ^1H and ^{15}N NMR studies showed that the problem of isomery in their

combinations is complicated also by the orientation of the oximic groups around the C – C axe [3, 4].

The dioximic structures in regard of their analytic capacity of application are a very interesting and also a very thoroughly examined field. The increasing interest in this class of compounds goes by itself, taking into account the broad variety of possibilities these organic binders, and the metallic complexes they build may provide. Of the many and diverse applications of asymmetric dioximes we would mention their use on a large scale as extraction agents, in diverse sampling processes, in the variations of both normal extraction and synergistic processes. Nowadays, the α -dioximes are found in the composition of some sensors, used for determining traces of Ni and Pd in the water of lakes, oceans, and of diverse biologic materials [5]. Also, the dioximes are used in a series of modern separation techniques, like the chromatographic methods (GC, HPLC) which are used for removing traces of transitional metals of diverse reagents. The additions of dioximes to the stationary phases, which are used by the chromatographic techniques substantially, contribute to the rise of resolution of separation by increasing the selectivity [6, 7].

EXPERIMENTAL

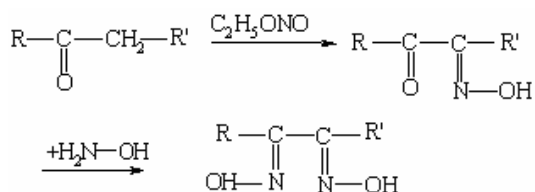
The dioximic structures can be obtained by isonitritization active of the methylene groups in vicinal position to the carbonyl group of the molecule of ketones. The synthesis steps are:

- monoxime first obtained by treatment with ethyl-ketone nitrite in concentrated mineral acid
- medium, then treated with NH_2OH transforming the ketoxime in the appropriate dioxime [8, 9].

In the present study our compounds were synthesized by palladium complexes with asymmetric dioximes: methyl-ethyl-dioxime, respectively methyl-isopropyl-dioxime. The palladium (II) complexes formed in acid medium at pH 2-4, as crystalline orange masses. The palladium complexes with asymmetric α -dioximes, similarly to other bivalent metals such as Ni (II) and Pt (II), have a planar-square structure stabilized by two intramolecular hydrogen bonds as presented in Fig. 1.

Groups R and R' influence the physico-chemical properties of asymmetric α -dioximes and their complexes. Synthesis of Pd (II) complexes with asymmetric aliphatic dioxime

2-25 mg of Pd^{2+} are dissolved in 50 ml water and acidified with dilute HCl to pH 2 - 4, by heating in



water bath to 80 - 90°C. Then 15 ml of 1 % dioxime in an alcohol solution are added. After 30 min the glass is cooled, then after a rest of 2-3 hours yellowish orange microcrystalline precipitate on a glass crucible G_3 is filtered. The precipitate is washed with hot water and dried in an oven at 160-180°C. Data for the element analysis of palladium complexes with methyl-ethyl-

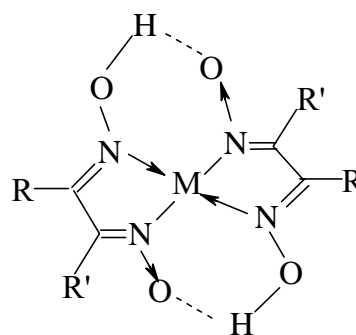


Fig. 1. Plane-square structure of the bivalent metal complexes with asymmetric dioximes, ($M^{II} = \text{Ni}, \text{Pt}, \text{Pd}$).

dioxime, respectively methyl-isopropyl-dioxime, are presented in Table 1.

RESULTS AND DISCUSSION

Spectrometric Determination of Pd (II) with Aliphatic Asymmetric Dioximes. 2-20 mg of Pd^{2+} are precipitated in acid medium in an aqueous solution with an excess of 1 % dioxime in alcoholic solution. The cooled mixture is extracted with acetone or chlorophorm. The extraction is repeated 3 - 4 times, each time with 10 ml of organic solvent. The organic phase is transformed into a graduated flask of 50 ml, and filled up to the mark with the extraction solvent. The absorption of the solutions is measured with a Cintra 101 spectrophotometer UV-VIS at 425 nm against the pure solvent. The calibration curves for the spectrometric determination of Pd(II) with aliphatic asymmetric dioximes are shown in Fig. 2 and Fig. 3.

Experimental data on the spectrometric determination of Pd (II) with aliphatic asymmetric dioximes were statistically fitted to a linear regression model (Tables 2 and 3).

The statistically processed data presented in Table 2, were used to the check calculations, namely:

$$\begin{aligned} \Sigma(x+y)^2 &= 1268.4140 \\ \Sigma x^2 + \Sigma y^2 + 2\Sigma xy &= 1268.4140 \end{aligned}$$

Table 1. The elemental analysis of palladium complexes.

Complex		% Pd	% C	% H	% N
[Pd(Me-Et-Diox.H) ₂]	Calculated	29.02	32.73	4.91	15.28
	Found	28.96	32.44	4.65	14.95
[Pd(Me-i-Prop-Diox.H) ₂]	Calculated	26.96	36.48	5.58	14.18
	Found	26.75	35.85	5.33	14.15

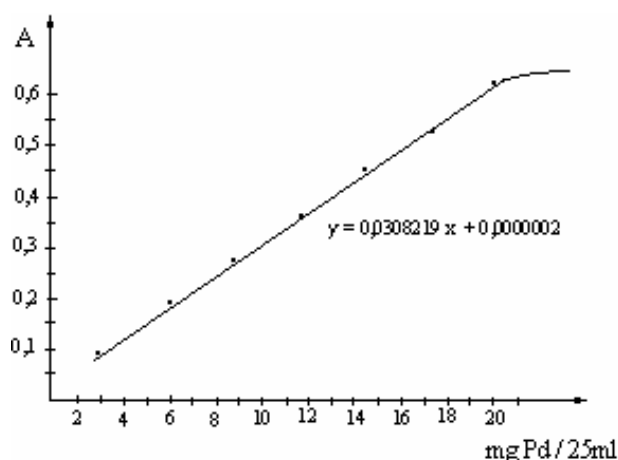


Fig. 2. Spectrometric determination of Pd (II) by precipitating as $[\text{Pd}(\text{Me-Et-Diox.H})_2]$.

We notice that the two values are very similar, which means that the method proposed for determining Pd(II) spectrometrically is reproducible and accurate.

The value of $r = 1$ shows that the results achieved through this method are reproducible, and the error may be neglected. The equations best described the dependence between the absorbance (A) and the active product concentration in the sample (mg), deduced through the linear regression, are:

$$1) y - \bar{y} = r \frac{\sigma_y}{\sigma_x} (x - \bar{x}) \quad y = 0.0000002 + 0.0308219 x$$

$$2) x - \bar{x} = r \frac{\sigma_x}{\sigma_y} (y - \bar{y}) \quad x = 0.0000001 + 32.4444444 y$$

The statistically processed data presented in Table 3 were used to check calculations, namely:

$$\Sigma(x + y)^2 = 1084.4795$$

$$\Sigma x^2 + \Sigma y^2 + 2\Sigma xy = 1084.4795$$

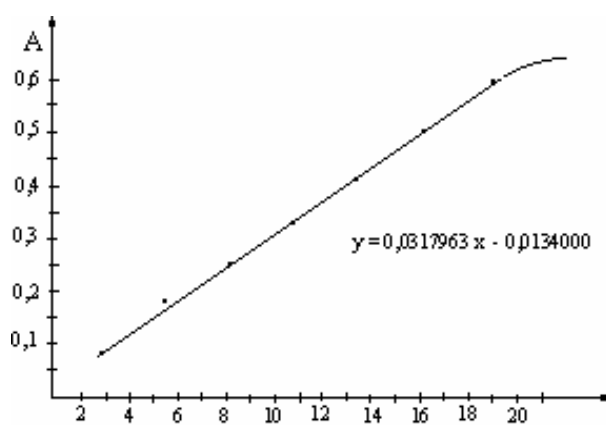


Fig. 3. Spectrometric determination of Pd (II) by precipitating as $[\text{Pd}(\text{Propox.H})_2]$.

We notice that the two values are equal, which means that the method proposed for determining Pd(II) spectrometrically is reproducible and accurate.

The value of $r = 1,01$ shows that the results achieved through this method are reproducible, and the error may be neglected.

The equations describing the dependence between the absorbance (A) and the active product concentration in the sample (mg), deduced through the linear regression, are:

$$1) y - \bar{y} = r \frac{\sigma_y}{\sigma_x} (x - \bar{x}) \quad y = 0.0317963 x - 0.013400$$

$$2) x - \bar{x} = r \frac{\sigma_x}{\sigma_y} (y - \bar{y}) \quad x = 0.2128235 + 32.0823529 y$$

The field of concentration of the Lambert-Beer law and the value of the absorption molar coefficient were checked for the case of the above mentioned determinations and are shown in Table 4.

Table 2. Spectrometric determination of Pd(II) after precipitation in the form of $[\text{Pd}(\text{metil-ethyl-diox.H})_2]$

No.	x	x ²	y	y ²	x.y	x+y	(x+y) ²
1	2.92	8.5264	0.09	0.0081	0.26280	3.01	9.0601
2	5.84	34.1056	0.18	0.0324	1.0512	6.02	36.2404
3	8.76	76.7376	0.27	0.0729	2.3652	9.03	81.5409
4	11.68	136.4224	0.36	0.1296	4.2048	12,04	144.9616
5	14.60	213.1600	0.45	0.2025	6.5700	15.05	226.5025
6	17.52	306.9504	0.54	0.2916	9.4608	18.06	326.1636
7	20.44	417.7936	0.63	0.3969	12.8772	21.07	443.9449
Total	81.76	1193.6960	2.52	1.1340	36.7920	84.28	1268.4140
$y = 0.0000002 + 0.0308219 x$; $x = 0.0000001 + 32.4444444 y$							

Table 3. Spectrometric determination of Pd(II) after precipitation in the form of [Pd(propox.H)₂].

No.	x	x ²	y	y ²	x.y	x+y	(x+y) ²
1	2.7	7.29	0.08	0.0064	0.216	2.78	7.7284
2	5.4	29.16	0.17	0.0289	0.918	5.57	31.0244
3	8.1	65.61	0.25	0.0625	2.025	8.35	69.7225
4	10.8	116.64	0.33	0.1089	3.564	11.13	123.8769
5	13.5	182.25	0.42	0.1764	5.670	13.92	193.1664
6	16.2	262.44	0.52	0.2500	8.100	16.70	278.8900
7	18.9	357.21	0.58	0.3364	10.962	19.48	379.4704
Total	75.6	1020.60	2.33	0.9695	31.455	77.93	1084.4795

$$y = 0.0317963 x - 0.013400 ; x = 0.2128235 + 32.0823529 y$$

Table 4. Linear concentration field and value of the molar absorption coefficient in the determinations of Pd (II) with aliphatic asymmetric dioximes.

Studied metallic complex	Linear concentration field (mg Pd)	Absorbion molar coefficient ϵ (l.cm ⁻¹ . mol ⁻¹)
[Pd(methyl-ethyl-diox.H) ₂]	0.1168-0.8176	280.941
[Pd(Propox.H) ₂]	0.1080-0.7560	302.81

CONCLUSIONS

This paper presents two new methods of analysis for determination of Pd(II) spectrometrically by using precipitation reagents of some aliphatic asymmetric α -dioximes. The statistical interpretation of the experimental data, in comparison with other methods which are known in the literature and we specially refer to the determinations based upon the reaction of palladium with dimethylglyoxime certify that the worked out methods of the present work are enough accurate and reproducible for the purpose we have in view. The asymmetric dioximes may set up potential organic reagents in the analytic determinations of palladium, as they are extremely sensitive and selective for this metal.

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