

gonadectomized litter-mate, the intact ovaries undergo hypertrophy<sup>3</sup> resulting in maturity of a large number of follicles<sup>4-6</sup>. This effect is due to hypersecretion of gonadotrophins<sup>7-10</sup>. DEC treatment arrested this increase in ovarian hypertrophy in both the moles studied possibly by inhibiting luteinizing hormone production as this hormone causes ovulation in rats. Since the number of mature Graafian follicles was also reduced it is possible that DEC interferes with the synthesis or release of both gonadotrophins of pituitary. However, further work is necessary to study its mechanism of action.

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## ACENAPHTHENEQUINONEDIOXIME AS AN ANALYTICAL REAGENT: STUDIES ON PALLADIUM COMPLEX.

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#### ABSTRACT

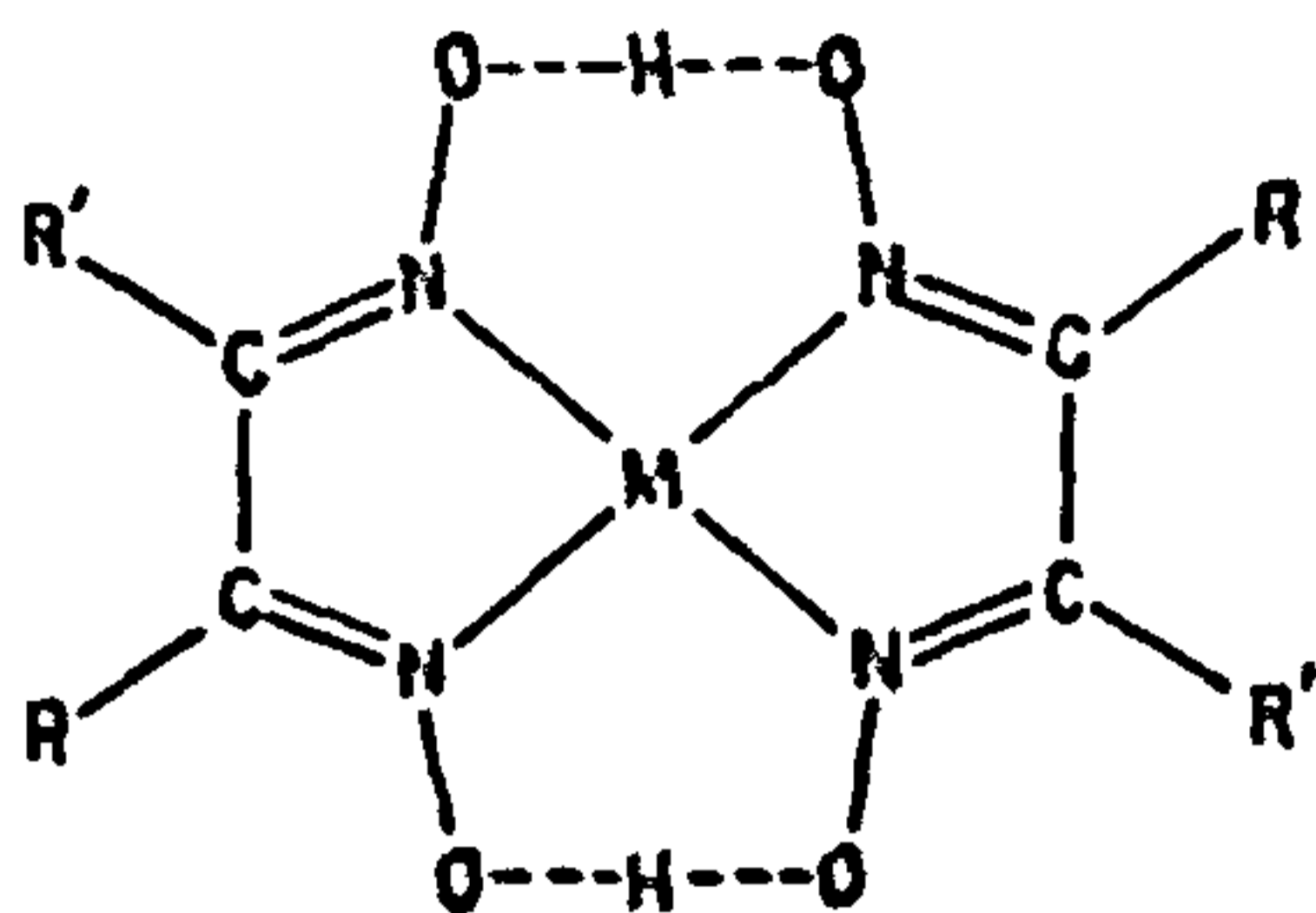
Acenaphthenequinonedioxime (ANDO) has been used as a reagent for gravimetric determination of palladium and for its separation from several cations and anions. Palladium is quantitatively precipitated by ANDO between the pH range 0.5-3.5. After drying the precipitate at 110°, its composition corresponds to the formula Pd(C<sub>12</sub>H<sub>7</sub>O<sub>2</sub>N<sub>2</sub>)<sub>2</sub>. Many commonly associated ions, except platinum and iron (III), do not interfere. Interference due to Fe(III) has been eliminated by masking it with excess citrate ion. Elemental analysis confirms the proposed metal:ligand ratio of the metal chelate. The complex is diamagnetic and gives typical *d-d* spectral bands as generally observed in square planar complexes involving d<sup>8</sup> electronic configuration. The involvement of strong hydrogen bridge and metal-nitrogen bond formation is confirmed by infrared and far infrared spectral analysis. Results of TG and DTA curves are also presented.

#### INTRODUCTION

VICINAL  $\alpha$ -dioxime has been used as an analytical reagent for transition metals, especially nickel and palladium, since its discovery and study of the selective properties of the dioximes<sup>1</sup>. Most transition metals form some kind of stable complex with these compounds. Usually the metal ion is coordinated to the functional group C(NO<sub>2</sub>)-

C(NO<sub>2</sub>) of the dioxime molecule, as shown in figure 1. The formation of four chelate rings will increase the stability of the complex<sup>2-4</sup>.

The present communication deals with the use of acenaphthenequinonedioxime (ANDO) as a gravimetric reagent for Pd(II). An ethanolic solution of the reagent reacts with Pd(II) at pH 0.5-3.5 quantitatively forming a brown complex of 1:2 stoichiometry analysing for Pd(C<sub>12</sub>H<sub>7</sub>O<sub>2</sub>N<sub>2</sub>)<sub>2</sub>. Pd(II)-oxime complex is



**Figure 1.** The structure of metal dioximes,  $M(AA)_2R$  and  $R'$  denote H, aliphatic or aromatic radicals.

insoluble in water, ethanol, methanol,  $CHCl_3$ ,  $CCl_4$ , benzene, ether etc.

### EXPERIMENTAL

All the chemicals used were of A.R. grade. The solution of Pd(II) was prepared by dissolving palladium chloride in 0.05 N HCl and standardised<sup>5</sup>.

The reagent was prepared by refluxing ethanolic solution of acenaphthenequinone with hydroxylamine hydrochloride (2 mol) and sodium acetate for 12 hr (MP  $224^\circ$ ) (literature value  $225^\circ$ ), IR spectra of the prepared dioxime were compared with those of the authentic sample (N found 13.29%; Calc. 13.21%).

An aliquot containing 25–40 mg of Pd was diluted to ~ 100 ml and the pH adjusted between 1 and 2 with hydrochloric acid. The contents were heated to  $60-70^\circ$  and treated with 0.5% ethanolic solution of ANDO added dropwise with constant stirring (4 mg ANDO for 1 mg Pd). The precipitate obtained was digested on a waterbath for 30 min and finally the solution was tested for complete precipitation. The precipitate was allowed to stand for 1 hr and filtered through G-4 sintered glass crucible. It was washed with distilled water several times until the precipitate was free from chloride. It was found that the precipitation of palladium is quantitative in the pH range 0.5–3.5. The conversion factor (metal/metal complex) is 0.2014. The relative standard deviation in the determination of Pd(20 mg) by the proposed method was  $\pm 0.35\%$  in 20 determinations. ANDO is suitable to estimate 20–50 mg of Pd(II).

The reagent has a favourable gravimetric factor (0.2014) compared to dimethylglyoxime (0.3168), salicyldoxime (0.2812), nioxime (0.2739), 4-methyl-nioxime (0.2558), resacetophenone oxime (0.2430) and 2-hydroxyl-1-naphthaldoxime (0.2223). The above oximes are, in general, widely used for gravimetric

estimation of palladium.  $Pd(ANDO)_2$  is less soluble than the complexes of the mentioned oximes and has a smaller Pd content, thus giving a larger weight of precipitate for a given weight of Pd.

The selectivity of ANDO as gravimetric reagent for Pd(II) was studied by determining 15–30 mg of Pd(II) in the presence of a number of other ions. An ion was considered to interfere if the weight of the metal chelate obtained differed by more than  $\pm 2\%$  from that for the calculated value. Foreign ions were added prior to adding the reagent solution and the pH value was adjusted in the range 0.5 and 1.5 Pt(IV) interfered seriously by forming a brownish black precipitate. In fact, ANDO is not selective for Pd(II) even in presence of 1 mg of Pt(IV). Interference due to Fe(III) was removed by using citrate ions; 3–4 g of tripotassium citrate rendered about 25 mg of Fe(III) innocuous. The tolerance limit of Cu(II) is however low. Common masking agents were used to improve the selectivity of the reagent for Pd(II) in the presence of large excess of Cu(II). The amount, indicated in the following section, offered a reliable result. The following ions, added as nitrate, sulphate or chloride, caused no interference on the M: Pd weight ratio given:

Zn(II)  $\geq 10$ ; Cd(II)  $\geq 12$ ; Hg(II)  $\geq 10$ ; Ag(I)  $\geq 9$ ; ;  
Be(II)  $\geq 12$ ; Al(III)  $\geq 15$ ; Th(IV)  $\geq 6$ ;  $UO_2(III) \geq 7$ ;  
Co(II)  $\leq 5$ ; Ni(II)  $\leq 5$ ; Pt(IV)  $\leq 0.05$ ; Rh(III)  $\leq 3$ ;  
La(III)  $\geq 13$ ; Sr(II)  $\geq 10$ ; Ba(II)  $\geq 12$ ; Zr(IV)  $\geq 12$ ;  
Mn(II)  $\geq 10$ ; Ca(II)  $\geq 13$ ; Cu(II)  $\geq 2$ ; Mg(II)  $\geq 10$ ;  
alkali metals  $\geq 20$ .

Among anions, phosphate, acetate, fluoride, bromide, carbonate, oxalate, citrate, tartrate, thiosulphate, borate and molybdate (added as alkali metal salts) do not interfere even when their weight is 10 times that of palladium.

#### Properties of $Pd(ANDO)_2$

Reports on elemental analysis are as follows. Found: C, 54.2; H, 2.89; N, 10.51; Pd, 20.11%.  $Pd(C_{12}H_7O_2N_2)_2$ . Required: C, 54.5; H, 2.65; N, 10.60; Pd, 20.14%. The palladium complex was experimentally diamagnetic. This study points to the square planar stereochemistry of the metal complex. Its nujol mull electronic spectra over the spectral range 300–1000 nm was recorded which show typical  $d-d$  spectral bands as generally observed in square planar complexes involving  $d^8$  electronic configuration. The broad band in the range 460–475 nm is probably due to two spin-allowed transitions  $^1A_{1g} \rightarrow ^1B_{1g}$  and  $^1A_{1g} \rightarrow ^1E_{1g}$  and the shoulder near 625 nm is due to  $^1A_{1g} \rightarrow ^1A_{2g}$  transition<sup>6-8</sup>.

IR spectra of acenaphthenequinonedioxime and its palladium complex were taken in potassium bromide

with the spectrophotometer (spectra in nujol mulls showed the same features). The ligand shows strong and broad absorption band in the infrared characteristic of a (-OH) stretching at  $3250\text{ cm}^{-1}$  and provided evidence for strong hydrogen bonding. The disappearance of this band in the complex points to the replacement of hydrogen from (-OH) group by the metal.<sup>9-11</sup>

The next group of bands appear at 1425 (hump) and 1360 (sharp) for the ligand. They shift to a higher frequency region in the metal complex and appear at  $1525\text{ cm}^{-1}$  (sharp) and  $1440\text{ cm}^{-1}$  (medium sharp). These may be due to asymmetric and symmetric C=N stretching vibrations respectively<sup>12,13</sup>.

Two sharp bands are observed in the region of  $900\text{--}1000\text{ cm}^{-1}$  and are precisely located at 990 and  $940\text{ cm}^{-1}$  for the ligand. They shift to a higher frequency region in  $\text{Pd(ANDO)}_2$  and appear at 1060 and  $1035\text{ cm}^{-1}$  respectively. These bands may be assigned to N-O stretching vibrations. The most important bands expected to appear in the region  $200\text{--}600\text{ cm}^{-1}$  are those due to metal-nitrogen stretching vibrations.  $\text{Pd(ANDO)}_2$  has a medium sharp absorption band at  $560\text{ cm}^{-1}$  which is assignable to the Pd-N stretching vibration<sup>14</sup>. Both the ligand and the metal complex absorb strongly at  $430\text{ cm}^{-1}$ . But the complex shows two additional bands at 325 and  $290\text{ cm}^{-1}$  which may be attributed to  $\pi(\text{Pd-N})$  and  $\delta(\text{Pd-N})$  type contributions<sup>15</sup>.

Very pure and dried metal complex was taken for recording TG and DTA studies. The TG curve indicates that there is no loss in weight upto  $150^\circ\text{C}$ . The compound mainly decomposes in three steps: first, a gradual loss in weight is observed from  $260\text{--}360^\circ\text{C}$ . From  $360\text{--}370^\circ\text{C}$  the weight loss is very rapid and the compound gives a very sharp exothermic peak at  $\sim 370^\circ\text{C}$ . The last phase of decomposition occurs in the region  $370\text{--}500^\circ\text{C}$ , relatively slowly, with a maximum loss at about  $500^\circ\text{C}$  which corresponds to the formation of metal oxide. Two exothermic peaks are observed at  $410^\circ$  and  $470^\circ\text{C}$ . Relatively sharper and broader is that of higher temperature.

On the basis of elemental analysis, magnetic moment, electronic spectra, IR and far IR spectra, the following structure for  $\text{Pd(ANDO)}_2$  is suggested.

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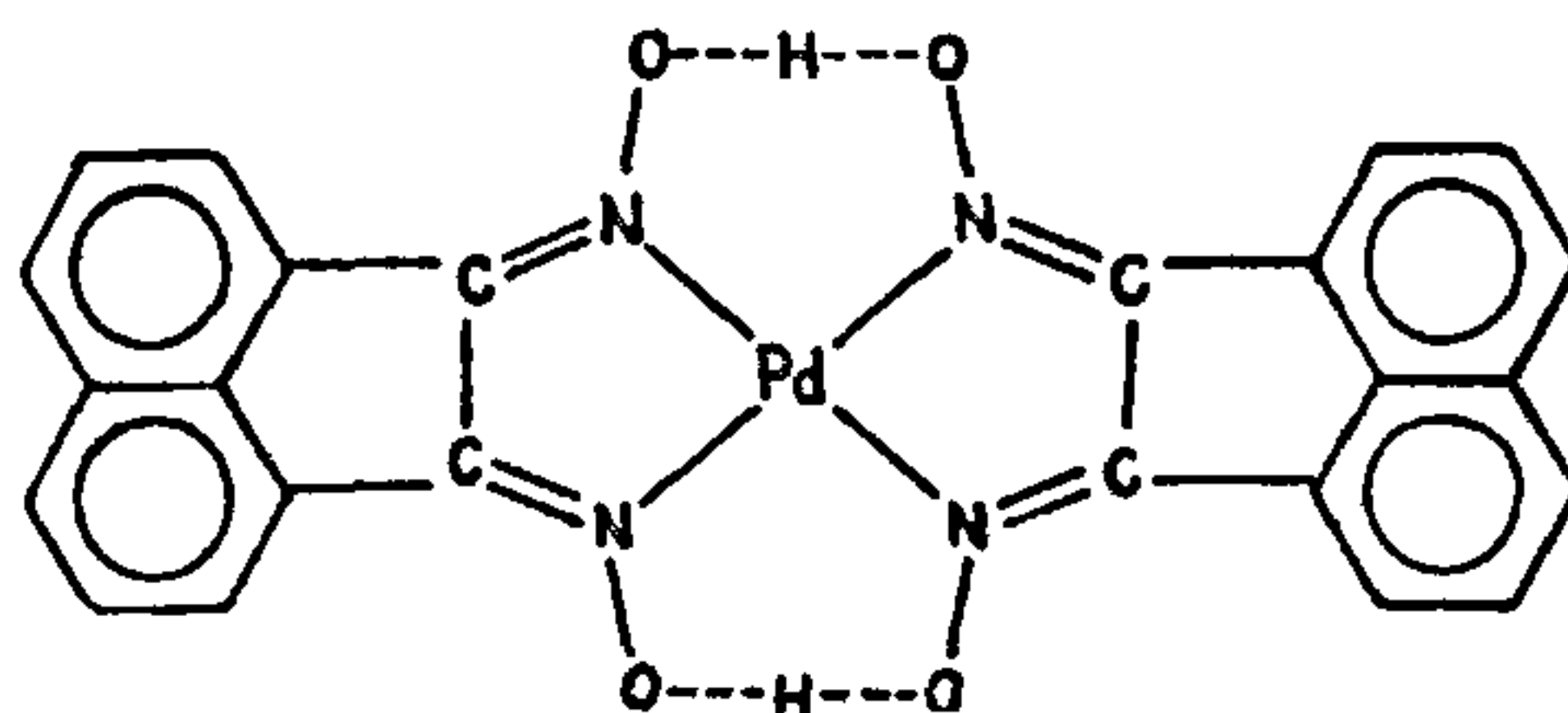


Figure 2. Bis (acenaphthenequinonedioximate) (Pd(II))

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