

List of Publications

1. Extraction and photometric determination of copper with substituted pyridines and thiocyanate, Indian Journal of Chemistry, 1982, 21A, 857-858.
2. Solvent extraction and spectrophotometric determination of palladium using mixed ligand complex formation with pyridine, α -picoline, β -picoline, γ -picoline or 2:4:6-collidine and thiocyanate, Indian Journal of Chemistry, 1983, Jan. Issue.
3. Extraction and spectrophotometric determination of cobalt with substituted pyridines and thiocyanate, Indian J. Chem. Soc. (communicated)
4. Extractive-gravimetric determination of Ni(II) and its separation from binary mixtures using pyridine and substituted pyridines in thiocyanate system.
Presented at the 70th session of Indian Science Congress, 3-8 Jan, 1983.
5. Substituted pyridines in Extractive-photometric determination of Ni(II), Cu(II), Co(II) and Pd(II).
Presented at National Symposium on Recent Trends in Microanalytical Chemistry, 27th-30th Dec., 1982, Presidency College, Calcutta.
6. Acenaphthenequinonedioxime as an Analytical Reagent: Studies on palladium complex.
Current Science (In press)

7. Acenaphthenequinonedioxime as an Analytical Reagent:
Studies on Nickel Complex.

Mikrochimica Acta (Revised and communicated)

Extraction & Photometric Determination of Copper with Substituted Pyridines & Thiocyanate

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Copper forms green coloured complexes in α -pic/ β -pic/ γ -pic/2,4,6-collidine-thiocyanate systems at pH 3-8. These are extractable into chloroform. The colour of the extract (stable at least for 24 hr) can be directly measured spectrophotometrically. The sensitivities are 0.0343, 0.0297, 0.031 and 0.0392 $\mu\text{g Cu(II) cm}^{-2}$ and molar absorptivities 8.855×10^3 , 9.317×10^3 , 9.038×10^3 and 9.175×10^3 litre $\text{mol}^{-1} \text{cm}^{-1}$ for α -, β - and γ -picolines and 2,4,6-collidine respectively.

Copper forms a green complex in the presence of pyridine and thiocyanate. This fact has been used in developing gravimetric as well as colorimetric methods of estimation of copper¹⁻⁵. In the present note we report the results of our studies on the extraction behaviour of copper(II) in the presence of some substituted pyridines and thiocyanate. Based on these studies, a rapid and sensitive method for the extraction and spectrophotometric determination of trace amounts of the copper has been developed. The substituted pyridines used are α -, β - and γ -picolines and 2,4,6-collidine. The optimum conditions for extraction, effect of pH, reagent concentration and effect of diverse ions, etc. have been studied.

Absorbance measurements were carried out with the help of a Beckman Spectrophotometer model DU 2. A digital pH meter (ECL, pH 5651) was used for pH measurements. Chloroform (E. Merck), α -, β - and γ -picolines and 2,4,6-collidine (BDH) were distilled before use.

Procedure—An aliquot containing 3-30 $\mu\text{g Cu(II)}$ was mixed with 15 ml of 2% (w/v) aqueous ammonium thiocyanate followed by the addition of 1 ml (100%) of α -/ β -/ γ -picoline/2,4,6-collidine. The volume of the aqueous phase was made upto 20 ml with doubly distilled water and then it was equilibrated with 20 ml of chloroform by manual shaking for 5 min. The layers were allowed to settle and the absorbance of the chloroform extract was measured against a corresponding reagent blank. Extracted copper was determined from a previously prepared calibration curve.

The chloroform extract was shaken with anhydrous sodium sulphate prior to the absorption measurement step in order to remove any associated water droplets.

Copper(II) complex in chloroform shows absorption maxima at 410, 405, 400 and 420 nm in the cases of α -, β -, γ -picolines and 2,4,6-collidine respectively. All the optical density measurements were carried out at the corresponding absorption maxima. The reagents absorb insignificantly at these wavelengths. Study of extraction behaviour of Cu(II) over the pH range 1-11 shows that quantitative extraction occurs at pH 3.5-6.5, 3-7.5, 4-7.2 and 5.5-8 for α -, β -, γ -picolines and 2,4,6-collidine respectively. Above or below these pH values, the extractions were found to be incomplete.

Optimum conditions for estimation—Results of estimations with different samples containing varying amounts of Cu(II) indicate that the system obeys Beer's law over a concentration range of 2.5-30 $\mu\text{g Cu(II)}$ per ml in case of α -, β - and γ -picolines and 4-40 $\mu\text{g Cu(II)}$ per ml in the case of 2,4,6-collidine.

Cu(II) is quantitatively extracted into chloroform in a single operation when the layers are shaken for 2 min.

Variation of reagent concentration was tested at the corresponding pH, the other variables remaining the same. It was found that 1 ml of the respective reagents and 1.5 ml of 2% aqueous ammonium thiocyanate are sufficient to extract 40 $\mu\text{g Cu(II)}$. Amount of organic reagents below 0.75 ml and aqueous thiocyanate below 1 ml (2%) resulted in incomplete extraction. Higher concentration (1 ml for organic reagents and 1.5 ml for 2% aqueous thiocyanate) had no effect on extraction but it was avoided because of reagent economy.

The optical densities of chloroform extract containing 5-16 $\mu\text{g Cu(II)}$ were measured at different intervals of time. The colour of the complexes in chloroform was found to be stable for 24 hr. At the end of 30 hr, the absorbance values decreased by about 3%. Therefore, optical densities were measured within 24 hr of extraction in all subsequent measurements.

Effect of foreign ions—In order to study the effect of diverse ions on the extraction behaviour, 5-16 μg of Cu(II) was extracted and determined according to the general procedure in the presence of about 10 mg of foreign ion except in the cases of Ni(II) [1.81 mg Ni(II)], Pd(II) [1.77 mg Pd(II)], Pt(IV) [4.00 mg Pt(IV)] and I^- [2 mg I^-] where more than the amount indicated in the brackets caused serious interference. Interference due to Fe(III) and Co(II) was avoided by masking them with ammonium hydrogen fluoride in the aqueous phase. All attempts to remove the interference due to Hg(II) failed, and the presence of Cu(II) always

produced a low absorbance value. Thiosulphate, EDTA, citrate and oxalate interfered by completely preventing colour formation. This may be due to the fact that Cu(II) has a greater affinity for these complexing agents compared with the organic bases used for estimation. In α - β - γ -picoline-thiocyanate systems, the presence of Pd(II) always resulted in a higher absorbance value and this obstruction could not be removed even when excess of the reagents, i.e., amine and thiocyanate were added. Other foreign ions used in the study were Mg(II), Ca(II), Sr(II), Ba(II), Al(III), Rh(III), La(III), UO_2^{2+} , molybdate, tartrate, acetate, borate, phosphate, fluoride and bromide.

Determination of copper in alloys: (i) *Gun metal*—0.5 g of the alloy (analysed sample supplied by Bureau of Analysed Samples Ltd, U.K., containing 86.4% Cu, 1.3% Zn, 10.5% Sn, 1.02% Pb, 0.02% Fe, 0.11% P and 0.26% Ni) was taken and its tin and lead contents were separated as usual in the forms of metastannic acid and lead sulphate respectively. Tin and lead free filtrate was suitably diluted with doubly distilled water. Each time an aliquot of suitably diluted solution was taken to estimate copper by following the general procedure, mentioned earlier. Against the actual value of 86.4%, copper was found to be 86.5, 86.2, 86.1 and 86.0% when α -pic, β -pic, γ -pic and 2,4,6-collidine were used respectively in the general procedure of estimation.

(ii) *Cupro-nickel*—0.5 g of cupro-nickel (analysed sample supplied by Bureau of Analysed Samples Ltd, U.K., containing 67.4% Cu, 0.82% Fe, 0.81% Mn and 30.7% Ni) was dissolved into a mixture of 10 ml of distilled water, 1 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 . When the dissolution was complete, the solution was boiled to remove the oxides of nitrogen. It was then sufficiently diluted to estimate its copper content according to the general procedure. Prior to addition of thiocyanate and α - β - γ -pic./2,4,6-collidine to the metal ion solution, ammonium bifluoride solution was added to mask any trace amounts of free

iron. Against the actual value of 67.4%, copper was found to be 67.2, 67.1, 67.3 and 67.5% when α -pic., β -pic., γ -pic. and 2,4,6-collidine were used respectively in the general procedure.

(iii) *White metal*—1.0 g of the alloy (analysed sample supplied by Bureau of Analysed Samples Ltd, U.K., containing 4.10% Cu, 0.38% Zn, 84.0% Sn, 3.9% Pb and 7.5% Sb) was taken and its tin and lead contents were separated as usual in the form of metastannic acid and lead sulphate respectively. Tin and lead free filtrate was used for estimation of copper. Against the actual value of 4.1%, copper was found to be 4.15, 4.13, 4.09, 4.05% when α -pic, β -pic, and γ -pic. and 2,4,6-collidine were used respectively in the general procedure.

(iv) *Aluminium alloy*—1.0 g of the alloy (analysed sample supplied by Defence Metallurgical Research Laboratory, Ichapur, W.B., containing 2.34% Cu, 1.5% Fe, 1.2% Mg, 1.51% Ni, 0.02% Mn, 0.19% Si and rest Al) was dissolved in conc. HCl. Diluted solution was used to estimate copper with substituted pyridines and thiocyanate. Estimations were carried out in the presence of ammonium bifluoride in order to mask free iron. Against the actual value of 2.3%, copper was found to be 2.30, 2.36, 2.35 and 2.31% when α -pic., β -pic., γ -pic. and 2,4,6-collidine were used respectively.

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Solvent Extraction & Spectrophotometric Determination of Palladium Using Mixed Ligand Complex Formation with Pyridine, α -Picoline, β -Picoline, γ -Picoline or 2,4,6-Collidine & Thiocyanate

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Palladium forms complexes with pyridine/ α -picoline/ β -picoline/ γ -picoline/2,4,6-collidine in the presence of thiocyanate. These complexes are quantitatively extractable into chloroform and thus provide a method for the estimation of Pd(II). All the species absorb around 310 nm. The sensitivities are 0.0076, 0.0042, 0.0051, 0.0050 and 0.0055 $\mu\text{g Pd(II) cm}^{-2}$, and molar absorptivities of the complexes are 1.39×10^4 , 2.51×10^4 , 2.46×10^4 , 2.13×10^4 and 3.21×10^4 $\text{lit mol}^{-1} \text{cm}^{-1}$ for pyridine, α -pic, β -pic, γ -pic and 2,4,6-collidine systems respectively. Hg(II), Fe(III), Co(II) and Cu(II) interfere in every system, while Ni(II) interferes in all the systems except in α -pic-SCN and 2,4,6-collidine-SCN systems.

Use of pyridine-thiocyanate for extractive-photometric determination of various metals is well known¹⁻⁶. But the extractive behaviour of some bivalent metals with methyl substituted pyridines in thiocyanate system has not been studied. We have undertaken a systematic programme to study the extractive behaviour of Pd(II) with pyridine and some of its methyl substituted derivatives in thiocyanate system. Based on these studies, a few rapid and sensitive methods for the extractive and spectrophotometric determination of trace amounts of palladium have been developed. The substituted pyridines used are: α -picoline, β -picoline, γ -picoline and 2,4,6-collidine.

After studying the influence of pH, and concentrations of reagents on the colour formation,

the following procedure was adopted for the estimation of Pd(II).

Procedure—An aliquot containing 10-100 $\mu\text{g Pd(II)}$ was mixed with 1.5 ml of 2% (w/v) aqueous ammonium thiocyanate followed by the addition of 1 ml (100%) of pyridine/ α -pic/ β -pic/ γ -pic/2,4,6-collidine. An appropriate amount of dilute HCl/NaOH (0.1 N solution) was added and pH of the resulting solution was measured after extraction. The volume of the aqueous phase was made upto 20 ml with excess of doubly distilled water and then it was equilibrated with 20 ml chloroform by manual shaking for 10 min. The two layers were allowed to settle for 10 min and then separated. Finally, the volume of chloroform extract was made upto 20 ml with excess solvent and its absorbance was measured against a reagent blank. Extracted palladium was determined from a previously prepared calibration curve. The chloroform extract was shaken with anhydrous sodium sulphate prior to the absorption measurement step in order to remove any associated water droplets. All the experiments were carried out at 25-30°C. The details of the experimental procedure for different systems are given in Table 1.

pH of the solution plays an important role in the quantitative extraction of Pd(II) into the organic layer. Study of extractive behaviour of the metal over the pH range 0.5-10 shows that quantitative extraction occurs in the pH ranges 4.9-7.1, 3.5-7.0, 2.6-5.8, 4.9-6.6 and 1.2-2.1 for pyridine, α -picoline, β -picoline, γ -picoline and 2,4,6-collidine systems respectively. In all the cases, 1 ml of 100% base and 1.5 ml of 2% (w/v) NH_4SCN solutions were used. Above or below these pH values, the extractions were found to be incomplete. Different amounts of palladium were extracted, as described in the general procedure earlier, at the corresponding pH and the optical densities were measured. The aqueous phase after each extraction

Table 1—Details of the Extractive Methods†

Parameter	Base employed				
	Pyridine	α -picoline	β -picoline	γ -picoline	2,4,6-collidine
pH	4.9-7.1	3.5-7.0	2.6-5.8	4.9-6.6	1.2-2.1
λ_{max} (nm)	315	304	306	305	310
Molar absorptivity ($\text{lit mol}^{-1} \text{cm}^{-1}$)	1.39×10^4	2.51×10^4	2.46×10^4	2.13×10^4	3.21×10^4
Interfering ions	V(IV), molybdate, $\text{S}_2\text{O}_3^{2-}$, Th(IV)	V(IV), molybdate, $\text{S}_2\text{O}_3^{2-}$	V(IV), molybdate, $\text{S}_2\text{O}_3^{2-}$	V(IV), molybdate, $\text{S}_2\text{O}_3^{2-}$	Pt(IV), V(IV), molybdate, borate, $\text{S}_2\text{O}_3^{2-}$

†Concentration of SCN was 1.5 ml (2% w/v) and that of the base 1.0 ml (100%) in each case.

was clear and colourless. The Beer's law was obeyed in the ranges 0.8-7.7, 0.4-4.52, 0.5-5.5, 0.5-5.0 and 0.5-5.5 μg of Pd(II)/ml CHCl_3 for the pyridine, α -picoline, β -picoline, γ -picoline and 2,4,6-collidine systems respectively. Pd(II) was quantitatively extracted into chloroform in a single operation when the layers were shaken for 10 min.

Effect of the variation of concentrations of the reagents was tested at the corresponding pH, the other variables remaining the same. It was found that 0.5 ml of the respective reagents and 1.3 ml of 2% (w/v) aqueous ammonium thiocyanate was sufficient to extract 100 μg Pd(II). Higher concentrations [1 ml for organic reagents and 1.3 ml for 2% (w/v) aq. ammonium thiocyanate] did not affect extraction, but were avoided because of reagent economy.

Sensitivities, in terms of Sandell's definition, are 0.0076, 0.0042, 0.0051, 0.0050 and 0.0055 μg Pd(II) cm^{-2} for pyridine, α -picoline, β -picoline, γ -picoline, 2,4,6-collidine systems respectively.

The optical densities of the chloroform extracts, containing 40-160 μg Pd(II) extracted by the recommended procedure, were measured at the different intervals of time and it was found that organic extracts always produced a steady absorbance value for at least 24 hr at room temperature. At the end of 35-40 hr, the absorbance values decreased by about 5-10%. So it seems convenient to measure the optical densities within 24 hr of the extraction.

Effect of diverse ions—In order to study the effect of diverse ions on the extraction behaviour, 40-100 μg Pd(II) was extracted and determined according to the general procedure in the presence of about 10 mg of foreign ions except in the cases of Rh(III) (1.96 mg), Pt(IV) (1.00 mg), Cd(II) (3.2 mg), F^- (4.5 mg), Br^- (5.8 mg), I^- (8.2 mg) and EDTA (4 mg) where more than the amount indicated in the brackets caused serious interference. Interference due to Fe(III) and Co(II) was avoided by masking them with ammonium hydrogen bifluoride in the aqueous phase, 5.38 mg of Fe(III) and 4.99 mg of Co(II) could be rendered innocuous in this way for each of the systems.

In each case, upto 7.68 mg Hg(II) could be masked by excess EDTA, and 6.014 mg citrate ions could render 2.13 mg of Cu(II) innocuous. Ni(II) interfered only with pyridine/ β -pic/ γ -pic-thiocyanate systems. When the methyl group is in the 2-position of the pyridine ring, Ni(II) does not form a complex with it; therefore, α -Pic and 2, 4, 6-collidine can be used to separate Pd(II) from Ni(II) without using any other masking agent. Interference due to Sr(II), Ba(II), Zn(II) and Cd(II) in the 2,4,6-collidine-thiocyanate system was successfully avoided by using aqueous ammonium hydrogen bifluoride. In the same system, Pt(IV) always co-extracted with Pd(II), and so in its presence Pd(II) could not be determined. Due to steric factors, 2,4,6-collidine requires highly acidic medium for complexation, and in relatively highly acidic solution only the ions Ba(II), Zn(II), Sr(II) and Cd(II) interfere; thus this system differs markedly from other four systems.

Molybdate and thiosulphate interfered in the extraction of Pd(II) from aqueous phase to the organic phase. Tolerance limit for oxalate in the case of pyridine-SCN and 2,4,6-collidine-SCN systems is relatively low. In these systems, only upto 4.5 mg of oxalate ions do not hamper the quantitative extraction of Pd(II).

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73. Substituted Pyridines in Extractive-Photometric Determination of Ni (II), Cu(II), Co(II) & Pd(II).

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Ni(II), Co(II), Cu(II) and Pd(II) form complexes with pyridine and methylsubstituted pyridines in the presence of thiocyanate. Cu(II) complexes, having λ_{\max} 400-420 nm, are extractable to chloroform quantitatively at pH 3-8. 2.5-40 μg Cu(II) can be determined by α -picoline, β -picoline, γ -picoline or 2:4:6-collidine and thiocyanate. Co(II) complexes are readily extractable into ethylacetate and absorb sharply at 620 nm. 3.5-40 μg Co(II) can be determined with sound accuracy with the above set of reagents. Pd(II) complexes with pyridine/ α -pic., β -pic., γ -pic. or 2:4:6-collidine and thiocyanate absorb around 310 nm, and 0.5-7 μg Pd(II) can also be determined in chloroform with the above reagents.

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 $\text{Pd}(\text{C}_{12}\text{H}_7\text{O}_2\text{N}_2)_2$. 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^8 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 α -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 dioximes¹. Most transition metals form some kind of stable complex with these compounds. Usually the metal ion is coordinated to the functional group C(NOH)-

C(NOH) of the dioxime molecule, as shown in figure 1. The formation of four chelate rings will increase the stability of the complex²⁻⁴.

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 $\text{Pd}(\text{C}_{12}\text{H}_7\text{O}_2\text{N}_2)_2$. Pd(II)-oxime complex is

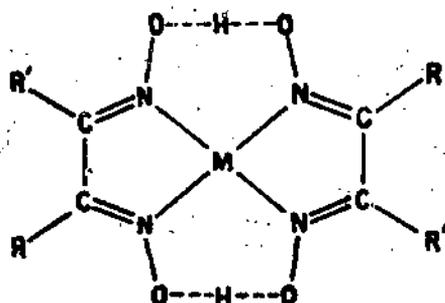


Figure 1. The structure of metal dioximes, $M(AA)_2R$ and R' denote H, aliphatic or aromatic radicals.

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 standardised⁵.

The reagent was prepared by refluxing ethanolic solution of acenaphthenequinone with hydroxylamine hydrochloride (2 mol) and sodium acetate for 12 hr (MP 224°) (literature value 225°), 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° 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), mioxime (0.2739), 4-methylmioxime (0.2558), resacetophenone oxime (0.2430) and 2-hydroxy-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) ≥ 10 ; Cd(II) ≥ 12 ; Hg(II) ≥ 10 ; Ag(I) ≥ 9 ; ;
 Be(II) ≥ 12 ; Al(III) ≥ 15 ; Th(IV) ≥ 6 ; UO₂(III) ≥ 7 ;
 Co(II) ≤ 5 ; Ni(II) ≤ 5 ; Pt(IV) ≤ 0.05 ; Rh(III) ≤ 3 ;
 La(III) ≥ 13 ; Sr(II) ≥ 10 ; Ba(II) ≥ 12 ; Zr(IV) ≥ 12 ;
 Mn(II) ≥ 10 ; Ca(II) ≥ 13 ; Cu(II) ≥ 2 ; Mg(II) ≥ 10 ;
 alkali metals ≥ 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(C₁₂H₇O₂N₂)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 *d⁸* electronic configuration. The broad band in the range 460–475 nm is probably due to two spin-allowed transitions ¹A_{1g} → ¹B_{1g} and ¹A_{1g} → ¹E_{1g} and the shoulder near 625 nm is due to ¹A_{1g} → ¹A_{2g} transition^{6,7}.

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 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.¹¹

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 cm^{-1} (sharp) and 1440 cm^{-1} (medium sharp). These may be due to asymmetric and symmetric C=N stretching vibrations respectively.^{12,13}

Two sharp bands are observed in the region of $900\text{--}1000\text{ cm}^{-1}$ and are precisely located at 990 and 940 cm^{-1} for the ligand. They shift to a higher frequency region in $\text{Pd}(\text{ANDO})_2$ and appear at 1060 and 1035 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. $\text{Pd}(\text{ANDO})_2$ has a medium sharp absorption band at 560 cm^{-1} which is assignable to the Pd-N stretching vibration¹⁴. Both the ligand and the metal complex absorb strongly at 430 cm^{-1} . But the complex shows two additional bands at 325 and 290 cm^{-1} which may be attributed to $\pi(\text{Pd-N})$ and $\delta(\text{Pd-N})$ type contributions¹⁵.

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°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°C which corresponds to the formation of metal oxide. Two exothermic peaks are observed at 410° and 470°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 $\text{Pd}(\text{ANDO})_2$ is suggested.

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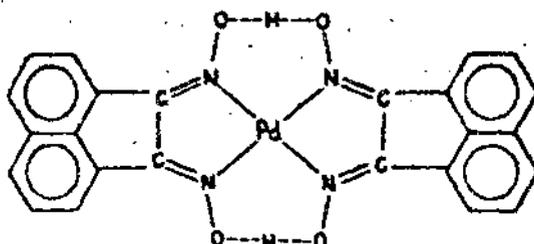


Figure 2. Bis (acenaphthenequinonedioximate) ($\text{Pd}(\text{II})$)

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- 14 Extractive-Gravimetric Determination of Nickel (II) and its Separation from Binary Mixtures Using Pyridine and Substituted Pyridines in Thiocyanate System.

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A procedure is described for extractive-gravimetric estimation of nickel (II) as pyridine/ β -picoline/ γ -picoline thiocyanates, and its separation from binary mixtures containing Cobalt (II), Copper (II) and palladium (II). Nickel (II) forms sky blue chloroform soluble complexes with pyridine/ β -picoline/ γ -picoline in thiocyanate system but fails to do the same when the methyl group is in the α -position of the pyridine ring. For quantitative complexation the required pH ranges are 5.0–6.8, 4.5–6.5 and 4.5–5.2 for pyridine-SCN, β -picoline-SCN and γ -picoline-SCN systems respectively. Ethyl acetate extracts quantitatively cobalt (II) and chloroform does similarly for copper (II) and palladium (II) leaving nickel (II) in the aqueous phase when α -picoline-SCN and 2:4:6 collidine-SCN are used as extractants. Cobalt (II), copper (II) and palladium (II) demand the pH ranges 3.5–7.5 & 0.5–8.0, 3.5–6.5 & 5.5–8.0 and 3.5–7.0 and 1.2–2.1 for α -picoline-SCN and 2:4:6 collidine-SCN respectively for complete separation.