

[(10–40 μg Pd (II)] is mixed with CHMAO (2 ml., 0.01 M ethanolic solution). The mixture was buffered to pH 2–4 and the total volume made upto 10 ml with water. The mixture was allowed to stand for about 100 min. and then extracted into 8 ml. of chloroform by vigorous shaking. The chloroform solution was separated and the absorbance recorded against the reagent blank prepared under similar conditions at 400 nm. The palladium content was found from the calibration curve.

Interferences.—The following ions did not cause a deviation in absorbance of more than 2.5% at pH 2.5–4.0 when present in amounts (ppm) shown in parentheses: Co (II) (500), Ni (II) (500), Cu (II) (300), Zn (II) (800), Mg (II) (800); Cd (II) (1000), MoO_2 (II) (500), UO_2 (II) (500), VO (II) (500), Hg (II) (500), Mn (II) (500), Sb (III) (400), Bi (III) (400), As (III) (400), Cl^- , Br^- , I^- , NO_2^- , $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-} , SO_3^{2-} and CO_3^{2-} upto (2000 each). But EDTA, Fe (III), and F^- interfere seriously even in small quantities.

Results and Discussion

Palladium forms yellow precipitate with CHMAO, which is extractable into chloroform easily. Vosburgh and Cooper's method⁵ shows the formation of only one complex and maximum absorbance lies at 400 nm. The absorbance *versus* pH plot shows that the absorption of the complex remains maximum and constant between pH 2.5–4.0 and pH 3.0 was maintained for these studies. Similarly absorbance *versus* reagent plot shows that at least four times excess of reagent is essential for complete precipitation.

The system obeys Beer's law upto 18 ppm of palladium and from Ringbom's plot is 5.00–16.20 ppm. The molar extinction coefficient is 2800 and its sensitivity is 0.038 μg Pd/cm².

Stoichiometry of the complex.—Job's method⁶, mole ratio method⁷ and slope ratio method⁸ showed that the metal and the ligand were present in 1 : 2 ratio in the complex.

Stability constant of the complex.—The conditional stability constant (27° C) was determined by (1) the mole ratio method and (2) Dey and Mukherji method⁹ and the log of stability constant was 8.44 and 8.76 respectively. The free energy of formation of the complex, $-\Delta F = RT \ln K$, was 11.86 Kcal/mole.

A number of oximes react with palladium (II) to give precipitate which are extractable into organic solvent like chloroform. Dimethylglyoxime¹⁰ is a selective reagent for separation of palladium (II) from other platinum metals. But the sensitivity is poor (0.06 μg Pd/cm²) at 375 nm. α -Furil-

dioxime¹¹ (sensitivity 0.005 μg Pd/cm² at 380 nm) and phenyl- α -pyridyl ketoxime¹² (sensitivity 0.0036 μg Pd/cm² at 410 nm) are sensitive and selective reagents for palladium (II). However, CHMAO (sensitivity 0.038 μg Pd/cm² at 400 nm) is more sensitive than dimethylglyoxime but less sensitive and selective as compared with the other oximes.

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PREPARATION MOLAR CONDUCTANCE AND INFRA RED SPECTRA OF SOME AROMATIC AMINE COMPLEXES OF COPPER (II) PHTHALIMIDE

Part I. Complexes of *o*-, *m*-, *p*-toluidines, piperidine and morpholine

THE above-mentioned amines have been used to prepare 5 new coordination complexes with copper (II) phthalimide, and their structures have been resolved on the basis of analysis, molar conductance and infra red measurements.

All the complexes were prepared by refluxing copper (II) phthalimide with amines in 1 : 2 ratio in acetone for 6 hours, and crystallising out the complex from solution by the addition of petroleum ether. These were recrystallised from methanol, dried and analysed.

(a) *Diphthalimidodipiperidine Copper (II)*—
[Cu (C₈H₇O₂N)₂ pip₂]^o. Found Cu = 13.90; C = 62.97; H = 5.89; N = 10.98%; Calculated Cu = 14.25; C = 63.34; H = 6.09; N = 11.34%.

TABLE I
Infrared absorption frequencies in Cm^{-1}

Complex	molar conduc- tance	NH stretching	NH ₂ deforma- tion	C-N stretching	H-C-C- wagging	H-N-C deforma- tion	>C=O stretching
(a) $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_2\text{N})_2(\text{pip})_2]^+$	0.37	3160 s	1470 s 1380 m 1300 m	850 m	1683 s
(b) $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_2\text{N})_2(\text{mor})_2]^+$	0.32	3210 s	1420 s 1370 m 1335 m	858 w	1691 s
(c) $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_2\text{N})_2(o\text{-tol})_2]^+$	0.33	3250 s	1600 s	1110 s	1680 vs
(d) $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_2\text{N})_2(m\text{-tol})_2]^+$	0.31	3220 s	1609 m	1109 s	1692 s
(e) $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_2\text{N})_2(p\text{-tol})_2]^+$	0.39	3270 m	1601 s	1095 s	1688 s

(b) *Diphthalimidodimorpholine Copper (II)*— $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_2\text{N})_2(\text{mor})_2]^+$ Found Cu = 12.57; C = 58.08; H = 4.88; N = 10.90%; Calculated Cu = 12.76; C = 57.88; H = 5.22; N = 11.25%.

(c) *Diphthalimidodi(o-toluidine) Copper (II)*— $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_2\text{N})_2(o\text{-tol})_2]^+$ Found Cu = 11.55; C = 66.62; H = 4.61; N = 9.96%; Calculated Cu = 11.81; C = 66.97; H = 4.82; N = 10.41%.

(d) *Diphthalimidodi(m-toluidine) Copper (II)*— $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_2\text{N})_2(m\text{-tol})_2]^+$ Found Cu = 11.67; C = 66.89; H = 4.51; N = 9.82%.

(e) *Diphthalimidodi(p-toluidine) Copper (II)*— $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_2\text{N})_2(p\text{-tol})_2]^+$ Found Cu = 11.98; C = 66.66; H = 4.92 and N = 10.02%.

Copper was estimated as cuprous thiocyanate, Carbon, hydrogen and nitrogen were estimated microanalytically. Conductivity values were determined in methanol solution (Conc. 10^{-3} M) with Philips PR 9500/90 instrument. I.R. spectra were recorded with nujol mulls on Perkin Elmer Spectrophotometer model 137. Details are given in Table I.

The molar conductance values for the complexes are in the range 0.3–0.6 and these confirm their non-electrolytic nature. It is thus indicated that both the amine and phthalimide ions are coordinated to the metal and the number of amine molecules coordinated is 2 for all the amines used.

In the i.r. spectra of the toluidine complexes the N–H stretching, NH₂ deformation and C–N stretching vibrations show considerable negative shift which has been taken as an evidence for co-

ordination through the nitrogen atom of the base¹⁻⁵. In the piperidine and morpholine complexes, the bands due to NH stretching vibrations show negative shift, but those due to H–C–C wagging and H–N–C deformation modes show positive shift, due to the coordination of the nitrogen atom of the amine⁶.

All complexes show one strong band at around $1685 \pm 10 \text{ cm}^{-1}$ which is assigned to be the >C=O stretching vibration, which shows a negative shift of the order of some 60 cm^{-1} when compared to free phthalimide. This is again taken as an evidence of the coordination of nitrogen of the phthalimide ion⁷⁻⁸.

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