TABLE 1 — PROTON-LIGAND FORMATION CONSTANTS OF 5,6'-DICARBOXY-4-HYDROXYAZOBENZENE AND FORMATION CONSTANTS OF ITS METAL COMPLEXES

Cation	log K_1				log K_2				log K_3			
	I	II	III	Av.	I	II	III	Av.	I	II	III	Av.
H+	—	—	—	13·19*	4·10	4·10	4·13	4·11	2·09	2·09	2·09	2·09
Zn(II)	13·10	13·20	13·26	13·19	10·10	10·10	10·00	10·07	—	—	—	—
Cu(II)	12·50	12·50	12·51	12·50	—	—	—	5·50†	—	—	—	—
Ni(II)	9·80	10·00	9·98	9·92	7·40	7·40	7·40	7·40	—	—	—	—
Co(II)	9·10	9·20	9·36	9·22	6·90	6·90	6·89	6·89	—	—	—	—

I = half integral method.   II = linear plot method.   III = pointwise calculations method.
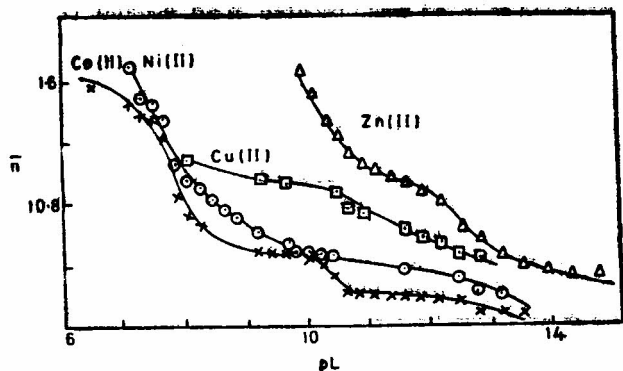*Obtained from $\bar{n}H = 1$.   †Obtained from $\bar{n} = 1$.

Fig. 1 — Formation curves for the metal complexes of 5,6'-dicarboxy-4-hydroxyazobenzene

of 6-carboxy group and nitrogen of the diazo group. The pH-metric titration indicates the possibility of complexation through oxygen atoms of the 4-hydroxy and 5-carboxy groups. However, the dissociation of protons from 6'-carboxy group cannot be ruled out. Though 6'-carboxy group is not involved in complex formation, the number of replaceable hydrogens are three. This is in accordance with Irving-Rossotti method where the term Y embodies all the replaceable hydrogens, through complex formation or self-dissociation. The term $\bar{n}H$ indicates the actual number of hydrogen atoms attached per ligand molecule at a particular value of B and which get replaced as a result of complex formation. The possibility of the complexation through 4-hydroxy and 5-carboxy groups finds further confirmation from the work of Drew and Fairbairn[13] who have stated that in the case of azo-salicylic acids, coordination of metal through azo-nitrogen is not possible.

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Spectrophotometric Determination of Pd(II) using Prochlorperazine Maleate as Reagent

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Prochlorperazine maleate forms a red coloured 1:2 (metal-ligand) complex with Pd(II) in the pH range 0·1 to 3·0. Beer's law is obeyed in the range of 0·2 to 12 μg Pd(II) with am olar extinction coefficient of 4·63 × 10^3 litre mole^{-1} cm^{-1} at 480 nm. The apparent stability constant of the 1:2 complex at pH 1·4 is $10^{11·2}$. The influence of some common ions is reported.

THE colour reaction between prochlorperazine maleate (PPM) and Pd(II) was employed for the identification of PPM[1-3]. The present paper describes the results of study of complex formation and a method for the determination of Pd(II).

PPM forms a red-coloured complex with Pd(II) instantaneously at room temperature, the stability of which depends on the pH of the reaction medium. Maximum absorbance was achieved in the pH range 0·1-3·0 for a solution containing 125 μg of Pd(II) and 5 ml of 0·1% PPM. A white turbidity or precipitate was formed, if the pH of the medium was above 3·5. The hydrochloric acid-sodium acetate buffer of pH 1·4 was chosen for all further work.

The volume of the buffer solution has no effect on the absorbance of 5 μg Pd(II) solution over the

range 3-8 ml. The order of addition of reagents was not critical. The colour intensity remained practically unchanged up to 60°. The development of full colour takes place immediately after mixing the reagents and remained constant thereafter for about 75 min. It was found that a five-fold molar excess of the reagent over Pd(II) was required in order to obtain maximum absorbance.

Beer's law was valid over the Pd(II) concentration range 0·2-12 μg. The optimum concentration range evaluated by Ringbom's method[4,5] was 0·8-11 μg. Errors were in general ±1%. A molar absorptivity of $4·63 \times 10^3$ litre mole^{-1} cm^{-1} was obtained at 480 nm.

The sensitivity of PPM is more than that of 8-mercaptoquinoline[6], methylglyoxime[6,7], salicylaldoxime[6,7] and diethazine hydrochloride[8] which have been proposed as sensitive spectrophotometric reagents for Pd(II). The sensitivity of PPM is less than that of phenyl-α-pyridylketoxime[6,7], pyridine-RBE[9], p-nitrosodimethylaniline[9] and 1,10-phenanthroline-RBE[9].

The method of Vosburgh and Cooper[10] was used to find out the number of complexes formed under the experimental conditions of the study. Only one sharp maximum was obtained around 480 nm in each case indicating the presence of only one complex. The red complex exhibits absorption maximum at 480 nm. The reagent does not absorb at this wavelength. All subsequent studies were performed at 480 nm.

A stock solution of Pd(II) was prepared by dissolving 1 g of Pd(II) chloride (M/s Johnson Matthey) in 500 ml of 1·0M hydrochloric acid and standardized gravimetrically by the dimethylglyoxime method[11]. Working solutions were made by suitable dilution of this solution.

A stock solution of PPM (M/s Sandoz Ltd, Switzerland) was prepared by dissolving 0·25 g of PPM in 250 ml of 0·1M hydrochloric acid and was standardized by the ceric sulphate method[12]. This was stored in an amber coloured bottle in a refrigerator.

Beckman model DB spectrophotometer with matched 1 cm optical cells was used for absorbance measurements. The pH of the solutions was measured (vs SCE) with a pH meter model L1-10 (M/s Electronic & Industrial Instruments, Hyderabad).

Recommended procedure for colorimetric determination — The sample solution containing 5-300 μg of Pd(II) was transferred to a 25 ml volumetric flask. To this was added 5 ml of 1M hydrochloric acid-1M sodium acetate buffer of pH 1·4 and 5 ml 0·1% PPM solution and the solution diluted to the mark with doubly distilled water. The solution was mixed thoroughly and the absorbance measured at 480 nm against a corresponding reagent blank. The Pd(II) concentration of the sample solution was read directly from a calibration curve.

Effect of diverse ions — Solutions of diverse ions of suitable concentrations were prepared using analytical grade reagents. The following amounts (μg per ml) of foreign ions were found to give less than 2% error in the determination of 5 μg of Pd(II) per ml: osmium(VIII), 10; platinum(IV), 4; ruthenium(III), 1; rhodium(III), 5; iridium(III), 8; iron (III), 2; cobalt(II), 80; nickel(II), 550; copper(II), 850; fluoride, 450; chloride, 800; bromide, 230; iodide,

0·5; nitrate, 1640; sulphate, 560; phosphate, 700; acetate, 720; oxalate, 600; citrate, 1600; tartrate, 1150 and EDTA, 2. Ag(I), Au(III) and thiosulphate interfere at all concentrations and, therefore, no tolerance limits could be determined.

Composition of the Pd(II)-PPM complex — Job's method of continuous variation[13,14] and mole ratio method[15] were employed to establish the composition of the complex. The composition determinations were made in a medium of constant ionic strength (0·1M sodium nitrate) at a pH value of $1·4 \pm 0·1$ and a temperature of $27° \pm 1°$. The absorbance values were measured at 480 nm. The results indicated the formation of 1:2 complex between the metal and the reagent.

The apparent stability constant values of the complex calculated from the absorbance data by (a) method of Foley and Anderson[16] modified by Mukherji and Dey[17] and (b) mole ratio method[15] were $11·2 \pm 0·1$ and $11·0 \pm 0·1$ respectively.

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Thiobenzoylacetone as an Extracting & Colorimetric Reagent for Ni(II)

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Thiobenzoylacetone can be used for the simultaneous extraction and direct spectrophotometric determination of Ni(II). Ni(II) can be extracted in the pH range 8·8-9·4 as a red coloured complex and measured spectrophotometrically at 500 nm. The Beer's law is valid in the concentration range 0·5-10 μg/ml of Ni(II). The complex is stable for 120 hr. 10 ml of $10^{-3}M$ reagent is adequate for quantitative extraction. Ni(II) can be selectively separated from mixture containing a large number of cations and anions.