

band observed in the brown complex corresponds to the lower band at  $1650\text{ cm}^{-1}$  of Pd (IAI) (IAI'). This band has been assigned to the N-coordinated isonitroso- $\beta$ -keto imine. It is important to note here that the C=O frequency of the O-coordinated isonitroso- $\beta$ -keto imine ligand occurs at a higher frequency compared to the N-coordinated isonitroso- $\beta$ -keto imine ligand. The band at  $3260\text{ cm}^{-1}$  assigned to N-H stretching mode of Pd (IAI)<sub>2</sub> agrees well with the higher frequency band observed in the I.R. spectra of the asymmetrically coordinated palladium (II), nickel (II) and copper (II) complexes of the same ligand. This band is also assigned to the N-coordinated isonitroso- $\beta$ -keto imine ligand. These evidences suggest that both the ligands are coordinated to palladium (II) through nitrogen donors of the isonitroso groups in the brown complex.

The proposed structure for the complex is further supported by comparing its electronic spectrum with that of Pd (IAI) (IAI') in the solid state. The assignment of the electronic spectral bands of Pd (IAI)<sub>2</sub> are given in Table I.

Unlike Pd (IAI)<sub>2</sub>, which shows four bands in the visible region, Pd (IAI) (IAI') shows a broad shoulder around  $21200\text{ cm}^{-1}$ , which may possibly be the expected *d-d* transition. The differences in

the electronic spectra of the two complexes also support the proposed structure for the former complex.

TABLE I  
Electronic spectral bands of Pd (IAI)<sub>2</sub> in mull

$\nu$ in $\text{cm}^{-1}$	Assignment
22700	Possibly a charge transfer band
20600	$1_{A_{1g}} \rightarrow 1_{E_{1g}}$ (sh)
18500	$1_{A_{1g}} \rightarrow 1_{B_{1g}}$
17000	$1_{A_{1g}} \rightarrow 1_{A_{2g}}$

The isolation of the present complex shows that the kind of chelate linkage isomer formed by the isonitroso- $\beta$ -keto imine ligands depends upon the physical conditions like temperature, solvent, etc.

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### 3, 5-DICHLORO-2-HYDROXYACETOPHENONE OXIME AS A CHELATING AGENT: STUDIES ON ITS PALLADIUM(II) CHELATE

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#### ABSTRACT

3, 5-Dichloro-2-hydroxyacetophenone oxime (DCHAO) has been found to be a good reagent for gravimetric estimation of palladium and for its separation from other ions. The composition and structure of the chelate are studied by microanalysis, pH metric titration, I.R. and Electronic spectra.

**O**-HYDROXY keto-oximes have been successfully used as chelating reagents. The gravimetric and spectrophotometric studies of the metal chelates in solution have been reported by several workers<sup>1-4</sup>. Gupta and Lal<sup>5-7</sup> have reported the physico-chemical studies on the chelates of Cu (II), Ni (II) and Co (II) with 3, 5-dichloro-2-hydroxyacetophenone oxime (DCHAO). In this communication, we report DCHAO as a gravimetric reagent for Pd (II). The composition and structure of Pd (II) chelate has been determined on the basis of micro-analysis, pH metric titration, I.R. and Electronic spectra.

#### EXPERIMENTAL

DCHAO was prepared as reported earlier<sup>5</sup>. An ethanolic solution (0.5%) of the ligand was

employed for the gravimetric studies. A solution of palladium chloride was prepared from B.D.H. (A.R.) sample in 0.05 M HCl and standardised gravimetrically. Solutions of other ions were prepared from reagent grade samples. NaOH solution (0.05 M) was used for the pH titration using systronic pH meter (type 322).

#### Determination of Palladium (II)

Metal ion solution (~20 mg) is diluted to 100-125 ml and the pH adjusted (1.0 to 5.0) with hydrochloric acid and ammonium hydroxide buffer, heated to 60-70° and treated with (0.5%) ethanolic solution of DCHAO dropwise with constant stirring (about double the theoretical amount). The precipitate (yellow) was digested on water-bath

for about half an hour. It was filtered while hot through sintered glass crucible (G-4), washed with hot water and finally with 60% ethanol, dried at 100–120° C to a constant weight. It has been found that palladium can be quantitatively determined in the pH range 1.5–4.0. The gravimetric factor (metal/metal complex) is 0.19544.

#### Study of Interference

The procedure was the same as in the absence of foreign ions. The interference of Cu (II) and Fe (III) has been removed by using EDTA and tartaric acid (masking agent) respectively. Excess (10–15 times) of cations like  $\text{UO}_2$  (II), Ni (II), Co (II), Zn (II), Cd (II), Mo (VI), Hg (II), Mn (II), Sb (III), Bi (III), As (III) and sufficiently large excess of anions like  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{PO}_4^{3-}$  citrate and tartrate do not interfere at pH 2.0.

From the solution containing both palladium and cobalt/nickel, palladium was first precipitated as above at pH 2.5 and from filtrate, cobalt/nickel was precipitated at pH 7.5 and 6.5 respectively as reported earlier.<sup>6</sup>

#### Accuracy of the Estimation

Palladium (6–50 mg) could be estimated with an accuracy of  $\pm 0.4\%$ . At lower concentrations of the metal (4–6 mg) the error was about 4% higher.

#### Analysis

Elemental analysis for  $\text{Pd}(\text{C}_8\text{H}_6\text{NO}_2\text{Cl}_2)_2$ : calculated N 5.14, Cl 26.08 and Pd 19.54%, found N 5.17, Cl 26.04 and Pd 19.58%.

#### pH Metric Titration

The titrations were carried out with the solution containing metal and the ligand in the ratio 1 : 0, 1 : 1, 1 : 2 and 1 : 3 with 0.05 M NaOH.

Figure 1 represents the change of pH with the addition of alkali to various systems. Since palladium solution was prepared in 0.05 M HCl, necessary correction was made while evaluating the composition. Curve A (1 : 0, metal : ligand) shows two inflexions at 5 and 7 moles of alkali due to complete neutralization of acid and precipitation of metal as hydroxide respectively.

Curve B (1 : 1, metal : ligand) shows a lowering of pH due to the liberation of proton from the hydroxyl group on complexation with palladium. It is assumed that (1 : 2, metal : ligand) complex is formed, hence one proton released and half of the metal ion remains in free state. Both the released proton and free metal require two moles of alkali and five moles of alkali are needed for the acid, therefore one inflexion is observed at about 7 moles of alkali. Curves C and D are also very similar

to Curve B and confirm the 1 : 2 complex formation in this case.

Metal ligand ratio is also determined by Fenger *et al.*<sup>8</sup> method and found to be 1 : 2.

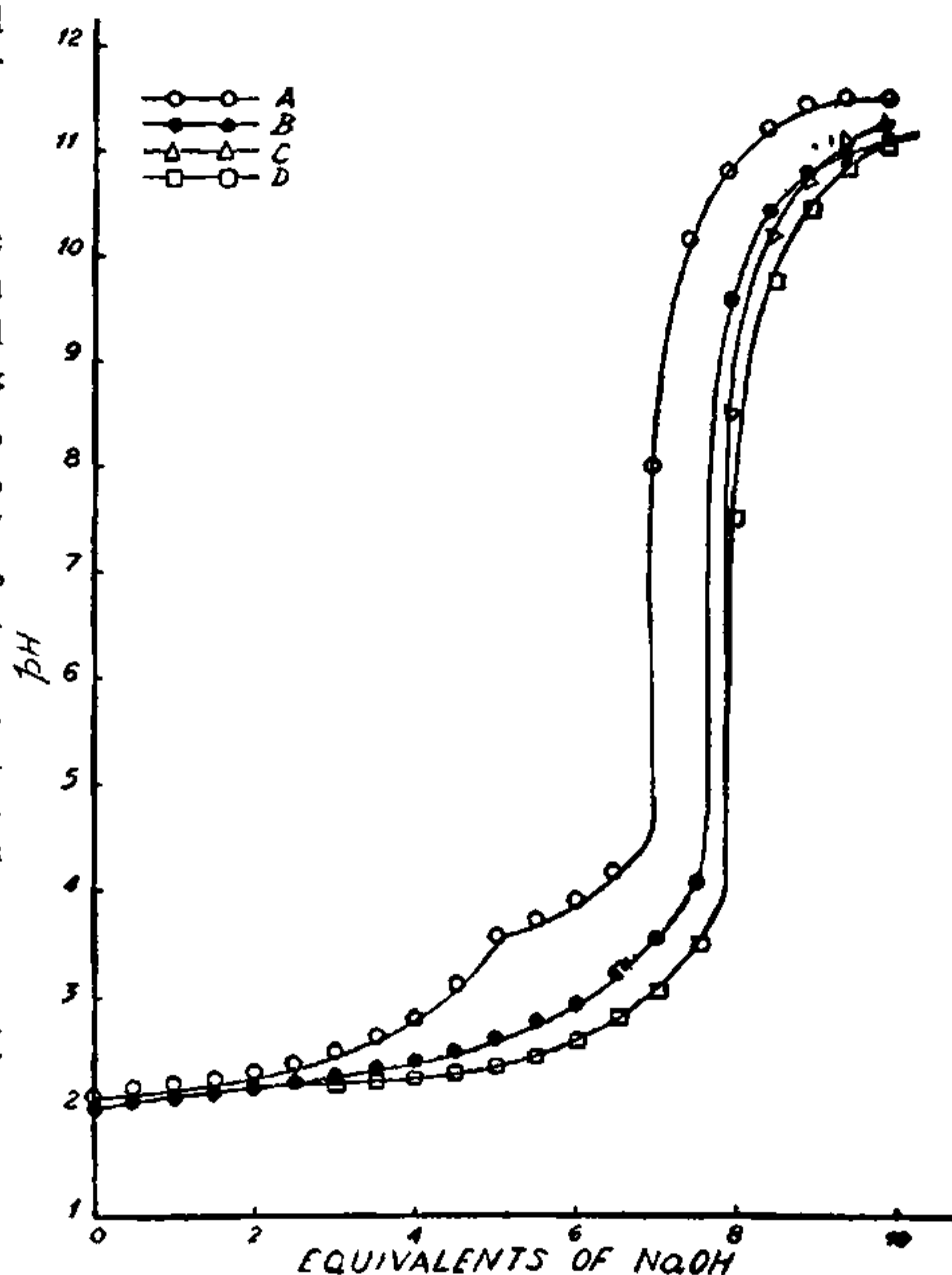


FIG. 1. pH metric titration of palladium chloride (5 ml,  $1 \times 10^{-2}$  M in 0.05 M HCl) with (0.05 M) NaOH. Curves A, B, C and D obtained in the presence of 0, 5, 10 and 15 ml of ligand (0.01 M) respectively, total volume 25 ml.

#### I.R. Spectra

I.R. spectra of the ligand and chelate were recorded from 4000–400  $\text{cm}^{-1}$ . In the ligand, two bands at 3333 and 3060  $\text{cm}^{-1}$  are assigned to intramolecularly bonded hydroxyl and aromatic C–H stretching frequencies respectively<sup>9</sup>, which shifts to 2850  $\text{cm}^{-1}$  in the chelate. The bands observed at 1580  $\text{cm}^{-1}$  and 1560  $\text{cm}^{-1}$  are due to C=N stretching and ortho substituted benzene ring vibration in the ligand. These two bands are coupled with each other and it seems reasonable to assume that the peak at 1560  $\text{cm}^{-1}$  is due to C=N stretching vibration, since these bands are lowered to 1532  $\text{cm}^{-1}$  in the chelate. The frequency arising at 1645  $\text{cm}^{-1}$  is ascribed to O–H deformation mode which is in good agreement with the results obtained by Ramaswamy *et al.*<sup>9</sup>. Very strong band at 1260  $\text{cm}^{-1}$  can be assigned to N–O stretching, and this shifts to 1230  $\text{cm}^{-1}$  in the chelate. Blinc and Hadzi<sup>10</sup>

explained the shift of N-O frequency to higher region on the basis of the contribution of polar structure of the ligand. The metal-nitrogen and metal-oxygen stretching vibrations have been recorded at 520 and 580  $\text{cm}^{-1}$  respectively.

Thus it is clear that on chelation hydrogen of hydroxyl group is replaced and nitrogen of oximino group donates a lone pair of electron to the metal ion.

#### Electronic Spectra

The ground state for the low spin complexes of  $d^8$  configuration is

$$[a_{1g}(z^2)]^2 [e_g(xy, yz)]^4 [b_{2g}(xy)]^2 \equiv {}^1A_{1g}$$

and are diamagnetic. The present DCHAO complex is also diamagnetic in nature. Three spin allowed  $d-d$  transitions are anticipated corresponding to transitions from the three lower lying  $d$ -levels to the empty  $d_{z^2-y^2}$  orbital; two electron transitions would be very weak and neglected. Energies corresponding to these transitions are determined from the following equations<sup>11</sup>:

$$d_{xy}(b_{2g}) \longrightarrow d_{z^2-y^2}(b_{1g}) E ({}^1A_{1g} \longrightarrow {}^1A_{2g}) \\ = \Delta_1 - C$$

$$d_{xy, yz}(e_g) \longrightarrow d_{z^2-y^2}(b_{1g}) E ({}^1A_{1g} \longrightarrow {}^1E_g) \\ = \Delta_1 + \Delta_2 - (3B + C)$$

$$d_{z^2} \longrightarrow d_{z^2-y^2}(b_{1g}) E ({}^1A_{1g} \longrightarrow {}^1B_{1g}) \\ = \Delta_1 + \Delta_2 + \Delta_3 - (4B + C)$$

Only two bands at 32010  $\text{cm}^{-1}$  and 44500  $\text{cm}^{-1}$  have been observed in the electronic spectra of  $\text{Pd}(\text{C}_8\text{H}_6\text{NO}_2\text{Cl}_2)_2$ . Following the assignment of Mason and Gray<sup>12</sup>, on the electronic spectra of the square planer  $[\text{Pd}(\text{NH}_3)_4]^{+2}$  complex, we may

presume that the former one is a combination of all the three spin allowed transitions. This means that in the case of Pd (II), complex, the values of ligand field parameters  $\Delta_1$ ,  $\Delta_2$  and  $\Delta_3$  derived from the  $d-d$  spectra of Pd (II) complex were found 35510, 1500 and 500 (in  $\text{cm}^{-1}$ ) respectively taking  $B = 500 \text{ cm}^{-1}$ ,  $C = 3500 \text{ cm}^{-1}$ . The other band at 44500  $\text{cm}^{-1}$  is due to the  ${}^1A_{1g} \rightarrow {}^1E_g$  transition<sup>13</sup>.

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## A SIMPLE AND ELEGANT TECHNIQUE TO ASCERTAIN FOOD ACCEPTABILITY AND MIGRATORY HABITS OF EARTHWORMS

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LITERATURE survey reveals that earthworms can use a wide variety of organic materials for their nutrition and propagation. The author and his colleagues had maintained in the laboratory colonies of earthworms for many years on a mixture of hay, weeds, kitchen waste and compost (which included animal dung)<sup>1</sup>. Evans and Guild<sup>2</sup> reported that earthworms produced more cocoons when fed on decaying animal products than those fed on plant materials. That earthworms can thrive well on animal dung has been known for a long time<sup>3,4</sup>. In fact, cowdung has been observed

to be superior to kitchen waste, straw, green manure, or even a mixture of all the four for the propagation of earthworms as well as from the point of view of increase in azotobacterial population, the latter being of presumable importance for the fixation of nitrogen in soil<sup>4</sup>.

Mention may be made in this context that Darwin<sup>5</sup> had reported on the behaviour of earthworms in relation to their selection of leaves for food as well as the manner in which the selected leaves get pulled to their burrows. It is known that earthworm can distinguish between different kinds of