

## 2,4-Dihydroxy-5-Nitropropiophenone Oxime as an Analytical Reagent: Studies on Ni(II) and Pd(II) Chelates

NITINKUMAR B. PATEL and K.K. DESAI\*

*Department of Chemistry  
South Gujarat University, Surat-395 007, India*

2,4-Dihydroxy-5-nitropropiophenone oxime (DHNPO) has been used as an analytical reagent for gravimetric and spectrophotometric determinations of Ni(II) and Pd(II). Metal : ligand ratio has been determined using spectrophotometric method. It is found to be 1 : 2 in both the complexes. Stability constants of complexes have been calculated. The Ni(II) and Pd(II) complexes were found to be having paramagnetic and diamagnetic character respectively. TGA studies were done on both complexes. Energy of activation for decomposition steps has been calculated using Broido method.

**Key Words:** 2,4-Dihydroxy-5-nitropropiophenone oxime, Ni(II) and Pd(II) chelates

### INTRODUCTION

In the current scenario of analytical, chemistry, many reagents are widely available. They include *o*-hydroxy ketoxime<sup>1-4</sup>, phenyl hydrazones, thiosemicarbazones, chalcone oximes, etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. In this work, we report the use of 2,4-dihydroxy-5-nitropropiophenone oxime (DHNPO) as a gravimetric reagent for Ni(II) and Pd(II). Spectrophotometric methods have been used to confirm the stoichiometry of complexes and to determine the stability constants of complexes.

### EXPERIMENTAL

All the spectrophotometric measurements were done on Bausch and Lomb spectrophotometer (Spectronic-20). All the pH measurements were done on ELICO pH-meter (LI-10T).

The reagent DHNPO was synthesized<sup>5</sup> and characterized by PMR spectra<sup>6-8</sup>.

### RESULTS AND DISCUSSION

**Gravimetric determination of Ni(II):** A 0.05 M solution of the reagent in 50% aqueous ethanol was used. Nickel sulphate solution (0.05 M, 10 mL) taken in a clean beaker was diluted to 100 mL with distilled water and pH of the solution was adjusted using ammonia, ammonium chloride buffer. The solution was

warmed at 60°C and small excess of reagent solution was added (0.05 M, 22 mL). A light green precipitate obtained was digested on a water-bath for 60 min at 60°C. The precipitate was filtered through a previously weighed sintered glass crucible ( $G_4$ ) and washed with warm water followed by 50% aqueous ethanol to remove excess of the reagent. The chelate was dried to constant weight at 110-115°C in a hot air oven, cooled and weighed. The experiment was repeated for different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH = 8.5 to evaluate its applicability. In any case the error did not exceed  $\pm 1.0\%$

**Gravimetric determination of Pd(II):** A 0.05 M solution of the reagent in 50% aqueous ethanol was used. Palladium chloride solution (0.01 M, 20 mL) taken in a clean beaker was diluted to about 100 mL with distilled water and desired pH was adjusted using hydrochloric acid-acetic acid buffer. The solution was warmed at 60°C and small excess of reagent solution was added (0.05 M, 9 mL). The golden yellow precipitate obtained was digested on a water-bath for 60 min at 60°C. The precipitate was filtered through a previously weighed sintered glass crucible ( $G_4$ ) and washed with warm water followed by 50% aqueous ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115°C in a hot air oven, cooled and weighed. The experiment was repeated for different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH = 2.5 to evaluate its applicability. In any case the error did not exceed  $\pm 1.0\%$ .

**Interference:** In gravimetric determinations of 29.35 mg Ni(II) at pH 8.5, 8-10 mg of Sr(II), Ca(II), Mg(II), Zn(II), Ba(II), Pd(II), Cd(II) and Al(III) did not interfere but Mn(II), Co(II) interfered seriously. Many common anions like nitrate, nitrite, sulphate, chloride, bromide, iodide were not found to interfere.

In gravimetric determinations of 21.28 mg Pd(II) at pH 2.5, 8-10 mg of Ca(II), Sr(II), Mg(II), Ni(II), Zn(II), Cd(II), Na(I), K(I), Ba(II) were not found to interfere but Fe(III) and Cu(II) interfered seriously. Many common anions like chloride, bromide, iodide, sulphate, nitrate, nitrite were not found to interfere.

### Spectrophotometric study of Ni(II)-DHNPO and Pd(II)-DHNPO complex

It was found that Ni(II) and Pd(II) complex with DHNPO absorbs maximum at 520 nm and 550 nm respectively, and hence all spectrophotometric measurements were done at these wavelengths.

Different aliquots of Ni(II) solution were taken. Buffer solution was added to maintain pH = 8.5. The excess of reagent was added to get precipitate of complex. It was extracted with three 5.0 mL portions of chloroform and the combined extracts were diluted to 25 mL. The absorbance was measured at 520 nm. The absorbances were plotted against the concentration of Ni(II). It was found that Beer's law was obeyed up to 24.66 ppm of Ni(II). Molar absorptivity and Sandell's sensitivity were calculated from graph and it was found to be  $2.31 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $0.254 \text{ } \mu\text{g of Ni(II)/cm}^2$  respectively.

Similarly Beer's law study was done for Pd(II)-DHNPO complex at pH = 2.5 and 550 nm. It was found that Beer's law was obeyed up to 21.28 ppm of Pd(II). Molar absorptivity and Sandell's sensitivity were calculated from graph and it

was found to be  $9.69 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $0.109 \mu\text{g of Pd(II)/cm}^2$  respectively.

Job's method<sup>9</sup> and mole ratio method<sup>10</sup> were used to determine the stoichiometry of the complex. It was found to be 1 : 2 (M : L) for Ni(II) and Pd(II) complexes. This is in agreement with the stoichiometry determined from gravimetry. The stability constants were calculated using the formula:

$$K_S = \frac{1 - \alpha}{4\alpha^3 C^2}$$

where  $\alpha$  = degree of dissociation given by  $\frac{E_m - E_s}{\bar{E}_m}$

C = concentration of complex

$E_m$  = maximum absorbance found from the graph

$E_s$  = absorbance at the stoichiometric molar ratio of the metal to reagent in complex

The average stability constant found from two methods for Ni(II) and Pd(II) complexes were found to be  $4.48 \times 10^9$  and  $4.49 \times 10^9$  respectively.  $\Delta G^\circ$  for complex formation at 27°C is  $-13.16 \text{ kcal/mol}$  for both the complexes.

TGA of the Ni(II) and Pd(II) chelate was done on Universal V<sub>1</sub>-12E-TA thermal analysis system. It was found that there is no loss in weight up to 175°C indicating that the chelate can be safely dried without decomposition at 110°C. Loss in weight above 175°C is due to decomposition of chelate and loss of ligand molecules. Weight of final residue corresponds to NiO and Pd metal found in case of Ni(II) complex and Pd(II) complex respectively are in accordance with the formula  $(\text{C}_9\text{H}_9\text{O}_5\text{N}_2)_2\text{Ni}$  and  $(\text{C}_9\text{H}_9\text{O}_5\text{N}_2)_2\text{Pd}$  respectively. The observed loss and weight of residue agree well with the loss and weight expected as per formula of chelate in which M : L ratio is 1 : 2 in the complexes.

Broido's method<sup>11</sup> was applied to TGA thermograms of Ni(II)-DHNPO and Pd(II)-DHNPO complexes obtained with heating rate 10°C/min. Activation energy  $E_a$  calculated using this method for thermal decomposition of chelates. The value of  $E_a$  was found as follows:

Step	Activation energy for Ni(II)-DHNPO complex (kcal/mol)	Activation energy for Pd(II)-DHNPO complex (kcal/mol)
I	-23.32	-18.11
II	-9.20	-17.69

The magnetic measurements of complexes at room temperature were carried out on Gouy balance as per the method suggested by Prasad and co-workers<sup>12</sup>. The magnetic moments of solid Ni(II)-DHNPO and Pd(II)-DHNPO complexes were determined, which indicated the paramagnetic and diamagnetic characters respectively. Values of magnetic moments at 4 amp and 6 amp for Ni(II)-DHNPO complex are 2.88 BM and 2.87 BM respectively. Effective magnetic moment value of Ni(II)-DHNPO complex indicates the presence of two unpaired electrons in *d*-orbitals.

The IR spectrum (in KBr pellets) of the ligand shows two bands in —OH stretching region. One band  $3399\text{ cm}^{-1}$  which disappears in the spectra of chelate is due to phenolic —OH group in 2-position. Examination of the IR spectra of the chelates shows that the band due to O—H stretching of 2-hydroxy group disappears in the Ni(II)-DHNPO and Pd(II)-DHNPO complexes. This indicates that during chelate formation, the hydrogen of 2-hydroxy group is lost and oxygen forms covalent bond with metal. The bands of aliphatic C—H stretching and aromatic C—H stretching are observed at nearly same positions in Ni(II)-DHNPO and Pd(II)-DHNPO complexes. The band due to the  $\nu(\text{C}=\text{N})$  stretching which is observed at  $1591\text{ cm}^{-1}$  in ligand is shifted to  $1540\text{ cm}^{-1}$  in complexes. This may be due to coordination of metal through nitrogen. This is also supported by slight downward shift of  $\nu(\text{NO})$  at  $9930\text{ cm}^{-1}$  in the ligand to  $930\text{ cm}^{-1}$  in the complexes. Thus in both the chelates metal is covalently bonded with oxygen and coordinate bonded with nitrogen.

### ACKNOWLEDGEMENT

The authors are thankful to the Head, Chemistry Department, South Gujarat University, Surat for the facilities provided to carry out the work.

### REFERENCES

1. K.K. Desai and H.B. Naik, *Indian J. Chem.*, **25A**, 297 (1986).
2. A.B. Bhatt and K.K. Desai, *J. Inst. Chem. (India)*, **63**, 5 (1991).
3. P.C. Trivedi and B.C. Haldar, *J. Indian Chem. Soc.*, **50**, 81 (1993).
4. P.A. Kahar and K.K. Desai, *Asian J. Chem.*, **10**, 910 (1998).
5. N.B. Patel and K.K. Desai, *Asian J. Chem.*, **14**, 1769 (2002).
6. C.M. Brewster and J.C. Harris, *J. Am. Chem. Soc.*, **52**, 4866 (1930).
7. R. Robinson and R.C. Shah, *J. Chem. Soc.*, 1490 (1934).
8. R.E. Omer and C. Hamilton, *J. Am. Chem. Soc.*, **59**, 643 (1937).
9. P. Job, *Ann. Chem.*, **115**, 332 (1938).
10. J.H. Yoe and A.L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).
11. A. Broido, *J. Polymer Sci., Part A-2*, **7**, 1761 (1969).
12. M. Prasad, S.S. Dharmati and S.V. Gokhale, *Proc. Ind. Acad. Sci.*, **20A**, 224 (1994).

(Received: 12 September 2002; Accepted: 15 November 2002)

AJC-2921

**38<sup>th</sup> NATIONAL MEETING OF THE  
JAPANESE CHEMICAL SOCIETY**

**TOKYO, JAPAN**

**MARCH 18–21, 2003**

**Contact:**

**E-mail: nenkai-help@chemistry.or.jp**