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Synthesis, Spectral and Thermal Studies of Ni(II) and Pd(II) Complexes with *p*-(N,N′-Dimethylaminobenzaldoxime)

B.H. MEHTA* and TANYA GUPTA
Department of Chemistry, University of Mumbai
Vidyanagari, Santacruz-East, Mumbai-400 098, India
E-mail: bipin_281050@yahoo.com

Ni(II) and Pd(II) are synthesized with the bidentate ligand *p*-(N,N′-dimethylaminobenzaldoxime). The synthesized metal complexes are further characterized by elemental analysis, molar conductance measurements, magnetic susceptibility measurements, infrared spectra UV-Visible spectral data and ^{1}H-spectra and thermal studies. Based on these characterizations the metal complexes of Ni(II) and Pd(II) may be formulated as ML_2 where M = Ni, Pd.

Key Words: Synthesis, Nickel(II), Palladium(II), Complexes, Oximes.

INTRODUCTION

In recent years, the coordination behaviour of organometallic compounds with several oxygen and nitrogen containing ligands as oximes has been studied extensively. As a consequence of their biological potency these complexes have received great attention[1, 2]. A number of oximic ligands have been reported for their bactericidal[3], fungicidal[4], antitumour[5] and sterease inhibiting[6] activities. Some of the oximes were used as chelating agents[7], analytical agents[8], for transition metal complexes and as catalysts[9, 10].

The detailed critical survey of the literature indicated that the nd^8 metal complexes with the ligand *p*-(N,N′-dimethylaminobenzaldoxime) are not reported with systematic investigations. It is, therefore, worthwhile selecting this ligand to study its complexing behaviour with Ni(II) and Pd(II) metals.

EXPERIMENTAL

All the chemicals, solvents and reagents used were of L.R. grade. The ligand *p*-(N,N′-dimethylaminobenzaldoxime) was prepared by treating an aldehyde with hydroxylamine hydrochloride in presence of sodium acetate trihydride which acts as a buffering agent[11]. The reaction mixture was refluxed for 2 h and poured in ice when the white oxime precipitated out. The oxime, thus obtained was washed with ice-cold distilled water, filtered, dried in an oven at 60°C and finally recrystallized from ethanol.

Nickel complex was synthesized by mixing aqueous solution of nickel sulphate (1 mg/mL) with an excess of the ethanolic solution of the ligand (1% w/v). The reaction mixture was digested on a water bath for about 1 h. Ni(II) formed light green coloured complex in the pH range 6.5–7.5. The product was filtered, washed with 20% ethanol and finally dried at 60°C in an oven.

Palladium complex was synthesized by mixing aqueous solution of palladium chloride ($PdCl_2$, 1 mg/mL) with an excess of the ethanolic solution of the ligand (1% w/v). On adjusting the pH of the reaction mixture between 3.5–4.0, a yellow colour was observed. The entire reaction mixture was then stirred vigorously for 0.5 h followed by refluxion for about 1 h. The complex separated as a yellow coloured solid which was then filtered washed, with aqueous ethanol (20%) and dried in an oven at around 60°C.

The elemental analysis of the ligand and the metal complexes was carried out by the methods reported in literature[12, 13]. The solubility of the complexes was checked in various polar and non-polar solvents like ethanol, methanol, acetone, chloroform, dimethylsulfoxide, tetrahydrofuran and acetonitrile. Molar conductivity of the ligand was recorded using 5×10^{-3} M solution in nitrobenzene on a Toshniwal conductivity meter. The electronic absorption spectra of the complexes were recorded in the UV-Vis region using THF as a solvent on a UV-Vis 2100 spectrophotometer supplied by M/s Shimadzu Corporation. IR spectra were recorded on FTIR-4200 supplied by M/s Shimadzu Corporation using KBr pellets. Magnetic susceptibility measurement was done using Gouy's method. The NMR spectra were recorded at RSIC, IIT, Mumbai on the VXR-300 S Varian spectrophotometer. Thermal analysis was carried out on STA-92 SETARAM thermobalance at TIFR, Mumbai.

RESULTS AND DISCUSSION

The physicochemical parameters of the ligand and the metal complexes are summarized in Table-1. The elemental analysis of the complexes suggests a 1 : 2 metal to ligand stoichiometry. It was recorded that divalent nickel and palladium complexes with nitrogen and oxygen donors can exhibit 1 : 2 metal to ligand stoichiometry[14, 15]. Mehta and Swar[16] have also reported diamagnetic Ni(II) and Pd(II) complexes with 1 : 2 metal to ligand stoichiometry. The metal complexes were examined for their solubility in various polar and non-polar solvents like water, alcohol, acetone, nitrobenzene, tetrahydrofuran, dimethylsulphoxide and dimethylformamide. The ligand *p*-(N,N′-dimethylaminobenzaldoxime) was freely soluble in most of the common organic solvents but the metal complexes had a limited solubility in various solvents. The Ni(II) and Pd(II) complexes were freely soluble in DMSO, DMF, THF and nitrobenzene but sparingly soluble in solvents like methanol, ethanol, chloroform[17]. The lower molar conductance values of 0.10 and 0.98 ($\times 10^{-3}$ siemens) in case of Ni(II) and Pd(II) complexes indicate their non-electrolytic behaviour. Rai *et al.*[18] have reported Ni(II) complex with the conductivity values of 0.14 (× 10^{-3} siemens) as non-electrolytic compounds.

TABLE-1
PHYSICOCHEMICAL PARAMETERS OF THE LIGAND AND METAL COMPLEXES

Ligand/ metal complex (Colour)	m.w.	m.p. (°C)	Elemental analysis (%)				Mol. cond. (× 10^{-3} siemens)
			C	H	N	M	
$C_9H_{12}N_2O$ (White)	164	144	65.85 (64.32)	7.31 (7.63)	17.07 (17.47)	—	3.21
$(C_9H_{11}N_2O)_2Ni$ (Light green)	384.69	220	56.14 (55.83)	5.71 (5.26)	14.55 (13.78)	15.25 (14.82)	0.10
$(C_9H_{11}N_2O)_2Pd$ (Yellow)	432.42	180	49.95 (49.27)	5.08 (4.63)	12.95 (11.69)	24.61 (25.28)	0.98

The Ni(II) and Pd(II) complexes were found to be diamagnetic in nature. Gul and Bekaroglu[19] have reported diamagnetic complexes of nickel and palladium with 1 : 2 metal-to-ligand stoichiometry.

The spectral data of the ligand and the metal complexes is summarized in Table-2. The infrared spectrum of the ligand exhibits sharp and strong absorption bands at a wavelength of 3242 and 1610 cm^{-1} which are characteristic bands for $\nu_{(O—H)}$ and $\nu_{(C=N)}$ respectively. The broad $\nu_{(O—H)}$ band at 3242 cm^{-1} disappears in the spectra of the metal complexes indicating deprotonation of the ligand and the involvement of oximic oxygen in bonding with the metal ions. The shift of the oxy-imine stretching vibration towards lower frequency suggests the involvement of oxy-imine nitrogen in coordination with the metal. Hankare *et al.*[20] and

TABLE-2
SPECTRAL DATA OF THE LIGAND AND METAL COMPLEX

Ligand/metal complex	Infrared spectral data (cm^{-1})					Electronic absorption band (cm^{-1}) ε = dm^3 mol^{-1} cm^{-1} × 10^4	
	ν(O—H)	ν(C=N)	ν(N—O)	ν(M—N)	ν(M—O)		
$C_9H_{12}N_2O$	3242	1610	956	-	—	33,333 (1.9)	42,735 (0.5)
						20,000 (10.25)	
$(C_9H_{11}N_2O)_2Ni$	—	1602	958	615	480	24,875 (17.17)	40,485 (2.85)
						32,573 (30.38)	
$(C_9H_{11}N_2O)_2Pd$	—	1600	962	680	484	22,421 (39.46)	
						38,387 (18.66)	41,322 (5.20)

Patel and Patel[21] have reported similar observations for the deprotonation of the ligand moiety and shift in these oxy-imine stretching vibrations during complexation. The absorption bands between 962 and 956 cm^{-1} are assigned to ν(N—O) stretching vibrations. The new absorption bands between 615–480 and 680–484 cm^{-1} in the spectra of the metal complexes may be assigned to ν(M—N) and ν(M—O) stretching vibrations in the far infrared region. Kipton *et al.*[22] have reported assignments to such ν(M—N) and ν(M—O) with bidentate ligands in the similar region.

The metal complexes are light green to yellow in colour. The electronic absorption spectrum of the ligand exhibits intense absorption bands at 33,333 cm^{-1}. The corresponding Ni(II) and Pd(II) complexes exhibit intense bands at 20,000 cm^{-1} ($^1A_{1g} \rightarrow {}^1E_g$), 24,875 cm^{-1} ($M \rightarrow L$) charge transfer, 32,573 cm^{-1}, 40,485 cm^{-1} (intraligand transitions), and 22,421 cm^{-1} ($^1A_{1g} \rightarrow {}^1B_{1g}$) and 38,387 cm^{-1} (π-π^*), and 41,322 cm^{-1} ($^1A_{1g} \rightarrow {}^1E_U$), respectively having high molar absorptivity. Hiremath *et al.*[23] have reported similar findings for nickel complex exhibiting sharp band at 30,348 cm^{-1}. Similarly, Jetley *et al.*[24] have reported intense absorption band for Pd(II) complex with 2-Hydroxy-3,5-dimethylacetophenone oxime at around 42,850 cm^{-1}.

The ^1H NMR spectral data of the ligand and the metal complexes is presented in Table-3.

TABLE-3

^1H NMR SPECTRAL DATA AND THERMAL DECOMPOSITION DATA

Ligand/ Metal complex	^1H NMR spectral data of Pd(II) and Ni(II) complexes in comparison with the oxime				Thermogravimetric data of the complexes			
	δ(C—H)	δ(C—HAr)	δ(C=NOH)	δ(N—$(CH_3)_2$)	Decomposition pattern of the metal chelates			Residue
$C_9H_{12}N_2O$	7.96 (s, 1H)	7.40–7.36 (d, 2H) 6.71–6.68 (d, 2H)	10.66 (s, 1H)	3.38 (s, 12H)	Temperature (°C) (% wt. loss)			Obs. (%) (cal. %)
$(C_9H_{11}N_2O)_2Ni$	7.96 (s, 1H)	7.83–7.80 (d, 2H) 7.40–7.36 (t, 2H) 7.16 (s, 2H) 6.71–6.68 (d, 2H)	—	3.37–2.94 (s, 6H) 2.92 (d, 6H)	260–280 (25.641)	480–500 (67.00)	520–800 (79.33)	79.33 (80.56)
$(C_9H_{11}N_2O)_2Pd$	7.96 (s, 1H)	7.83–7.80 (d, 2H) 7.40–7.37 (t, 2H) 7.16 (s, 2H) 6.71–6.68 (d, 2H)	—	3.37–2.94 (s, 6H) 2.92 (d, 6H)	200–220 (23.90)	360–380 (56.99)	720–740 (75.055)	75.39 (75.13)

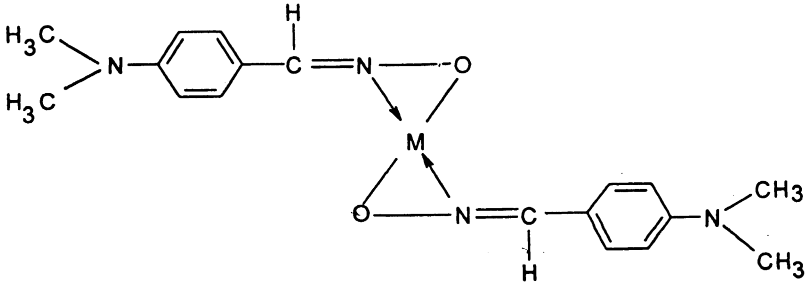
The spectrum of the ligand shows a signal at downfield of 10.66 ppm which is characteristic of oximic proton (=NOH). This signal is absent in the corresponding metal complexes indicating the disappearance of the oximic proton and the coordination of the metal ion to the nitrogen of the oxime. The spectrum of ligand exhibits multiple signals in the range of 7.40–6.68 ppm, which are characteristic signals for aromatic ring protons. The corresponding spectra of metal chelates also show a similar multiple of signals in the range with δ values in the range of 7.83–6.68 ppm. Similar assignments have been reported by Hodali *et al.*[25] and Mostafa *et al.*[26].

The thermogravimetric curves of the metal chelates do not exhibit any detectable change up to 200°C which suggests the absence of water of hydration as well as the coordinated water. The mass loss data of Ni(II) complex of *p*-(N,N′-dimethylaminobenzaldoxime) agrees with the loss of two ligand moieties in two different steps at decomposition temperatures at 280° and 500°C. Similar findings for Ni(II) complex are reported by Gaur and Sharma[27]. However, the TG data of Pd(II) complex indicate a three step decomposition process. The first and second steps of decomposition are probably due to the removal of organic moiety and the third step may be attributed to the conversion of palladium oxide to palladium metal in nitrogen atmosphere. The percentage loss at decomposition temperature in close agreement with the calculated values supports the interpretation. The overall decomposition process may be summarized as follows:

$$Ni(C_9H_{11}N_2O)_2 \xrightarrow{\Delta t,\ N_2} NiO$$

$$Pd(C_9H_{11}N_2O)_2 \xrightarrow{\Delta t,\ N_2} PdO \longrightarrow Pd$$

Thus, it may be concluded that the nickel and palladium complexes coordinate in 1 : 2 stoichiometry as indicated by elemental analysis measurements. The oxime *p*-(N,N′-dimethylaminobenzaldoxime) behaves as a bidentate ligand as it is evident from the IR spectral data. The coordination of the oxime to the metal ion is through both the donor atoms which is further supported by the absence of oximic proton in the ^1H NMR spectra of complexes. The diamagnetic behaviour of these complexes is indicative of their square-planar geometry which may be represented as follows:



M = Ni, Pd

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