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X-ray Crystallographic Studies of Nickel(II) and Palladium(II) Complexes of *o*-Hydroxy Acetophenone Oxime

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o-Hydroxyacetophenone oxime was synthesised by reacting *o*-hydroxyacetophenone with hydroxylamine hydrochloride. This oxime was used to synthesise nickel(II) and palladium(II) complexes having metal to ligand stoichiometry 1 : 2. The ligand and metal complexes were characterised by elemental analysis, molar-conductivity, electronic absorption and IR absorption spectra. The magnetic nature of the complexes was established using Gouy's balance method. The XRD data was used to index the compound for orthorhombic system with space group P_{mmm} or P_{222}.

INTRODUCTION

Organic chelating ligands containing oxime functional group have been extensively used in analytical chemistry for the detection and separation of metals.[1–3] Transition metal oxime complexes are reported to possess catalytic and biological activity.[4,5] The chemistry of metal oxime complexes is interesting since these species display an amazing variety of reactivity modes. Transition metal oxime complexes were studied using different spectroscopic techniques like UV-VIS and IR.[6] However, the elucidation of structure from X-ray diffractograms is not much attended. It is therefore worthwhile investigating the crystallographic nature of nickel(II) and palladium(II) complexes synthesised from *o*-hydroxyacetophenone oxime.

EXPERIMENTAL

All the chemicals and solvents used for the synthesis were of L.R. grade. *o*-Hydroxyacetophenone oxime was synthesized by treating *o*-hydroxyacetophenone with hydroxylamine hydrochloride using sodium acetate as buffer. The precipitate obtained was filtered and washed with water to remove excess of hydroxylamine hydrochloride. The oxime was recrystallised from aqueous methanol. The metal complexes were synthesized by mixing the methanolic solution of the ligand (1% w/v) with the metal solution (1 mg/cm^3). The pH of the reaction mixture was adjusted to 7 for nickel(II) complex whereas palladium(II) complex was precipitated at pH 3. The solid complexes obtained were filtered, washed with hot water and dried in oven at 60°C. The elemental analyses of ligand and complexes were carried out using reported methods[7]. The complexes were tested for solubility using various polar and non-polar solvents. Molar conductivity of the ligand and complexes were recorded using 10^{-3} molar solution on a Toshniwal conductivity meter and DMSO as a solvent. The electronic absorption spectra of complexes were recorded from their DMSO solution in the UV-visible region while diffused reflectance spectra were recorded using $BaSO_4$ as a diluent on

UV-VIS-2100 spectrophotometer supplied by M/s. Shimadzu Corporation. Infrared spectra were recorded on FTIR-4200 supplied by M/s. Shimadzu corporation using KBr pellets. The X-ray diffractograms were recorded on XRD-Shimadzu-6000 using CuK_α radiations (CuK_α, $\lambda = 1.5418$ Å). The X-ray diffractograms were scanned in the 2θ range of 5°–60°.

RESULTS AND DISCUSSION

The experimental findings on various investigations are summarized in Table-1. The ligand and metal complexes were crystalline in nature. The ligand is white in colour whereas the nickel(II) and palladium(II) complexes are green and yellow in colour respectively. The complexes are anhydrous in nature and stable at room temperature. The observed values of the elemental analysis are in close agreement with the calculated values for the metal complexes. Both the nickel(II) and palladium(II) complexes have metal to ligand stoichiometry 1 : 2. The complexes are sparingly soluble in common organic solvents but are sufficiently soluble in DMSO and nitrobenzene. The low values of the molar conductance ($7.8–9.6 \times 10^{-3}$ siemens) suggest the non-electrolytic behaviour of these complexes. The Gouy's balance method indicated that both the complexes are diamagnetic in nature, which points out the square-planar geometry of nickel(II) and palladium(II) complexes. Jetley and Singh[8] reported diamagnetic nature for nickel(II) and palladium(II) complexes for substituted *o*-hydroxy oxime. Agarwal and Agarwal[9] assigned square-planar geometry to nickel(II) and palladium(II) complexes derived from arylazo-bis-acetoxime ligand.

The characteristic IR absorptions of the ligand and their metal complexes are listed in Table-1. The ligand *o*-hydroxyacetophenoneoxime show the presence of characteristic ν(O—H) band at 3350 cm^{-1} and ν(>C═N) at 1640 cm^{-1}. This ν(O—H) band appears as a broad band in the region of 3100–2900 cm^{-1} for the nickel(II) and palladium(II) complexes. It indicates the involvement of phenolic oxygen in the bond formation with the metal ion[10]. The ν(>C═N) stretching vibrations in the respective complexes show bathochromic shift by 30–40 cm^{-1}, indicating the involvement of oximic nitrogen in coordination with the metal ion. In addition, the IR spectra show absorption band in the region of 610–580 cm^{-1} which can be assigned to ν(M—N) and ν(M—O) respectively[11]. Thus, the ligand coordinates to the metal ion through oximino nitrogen and phenolic oxygen after deprotonation, suggesting bidenate nature of the ligand.

The complexes were characterised with respect to various electronic transitions associated with it in the UV-visible spectal region. The nickel(II) complex shows strong absorption band in the region of 11,000 cm^{-1}, 16,000 cm^{-1} and 20,000 cm^{-1} which are assignable to d–d transitions. Khanolkar and Khanolkar[12] have reported three such d–d transitions for nickel(II) complexes of substituted acetophenone oximes in the similar region. The palladium(II) complex exhibit weak absorption bands around 22,000 cm^{-1} and 11,000 cm^{-1} and strong band around 27,000 cm^{-1} which are characteristic of d–d transitions[13]. The sharp band pointed in the region of 27,000 cm^{-1} in the spectrum of nickel(II) complex can be assigned to charge transfer transition, while palladium(II) complex exhibit such transition in the range of 33,000 cm^{-1}. The above spectral data indicates the square planar structure of

TABLE-1
ANALYTICAL AND SPECTRAL DATA OF LIGAND AND METAL COMPLEXES

Compound	Molar conductivity $\times 10^{-3}$ siemens	Elemental analysis (%)				Electronic absorbance (cm^{-1}) ($\varepsilon \times 10^3$ dm^3 $mole^{-1}$ cm^{-1})		IR spectral data (cm^{-1})			
		C	H	N	M	UV-visible	Reflectance	ν(O—H)	ν(> C═N)	ν(M—N)	ν(M—O)
$C_8H_9O_2N$	6.8	63.02	5.46	9.08	–	32,733	–	3350s	1640s	–	–
(*o*-Hydroxy-		(63.53)	(6.00)	(9.26)		(3.57)					
acetophenone						39,215					
oxime)						(8.13)					
$Ni(C_8H_8O_2N)_2$	7.8	52.60	4.81	7.10	15.65	26,315	11,363				
		(53.51)	(4.49)	(7.80)	(16.35)	(3.32)	16.025	2900b	1600s	610	450
						33,333	20,000				
						(9.37)	31,250				
$Pd(C_8H_8O_2N)_2$	9.6	46.70	3.64	6.21	25.70	27,777	11,627	3100b	1610s	580	475
		(47.28)	(3.96)	(6.89)	(26.12)	(5.08)	22,727				
						31,250	26,315				
						(6.77)					
						42,462					
						(42.94)					

nickel(II) and palladium(II) complexes which is supported by their diamagnetic nature.

The good quality of X-ray diffractograms of nickel(II) and palladium(II) complexes indicates high crystallinity of these complexes. The major refluxes were measured and corresponding 'd' values were obtained using Bragg's equation ($n\lambda = 2d \sin \theta$). The independent indexing of major refluxes was carried out using least square method. The miller indices h, k, l were calculated and refined by using Back-Cal program on computer. The nickel(II) and palladium(II) complexes can be successfully indexed to orthorhombic crystal system with formula factor (Z = 4) for palladium(II) complex and (Z = 8) for nickel(II) complex.

TABLE-2

CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR $Ni(C_8H_8O_2N)_2$

a (Å) = 9.7615 ± 0.0143
b (Å) = 9.9295 ± 0.0198
c (Å) = 38.6343 ± 0.0864
$\alpha = 90°$
$\beta = 90°$
$\gamma = 90°$

Volume ($Å^3$) = 3744.7310
D_{cal} (g/cm^3) = 1.27
D_{obs} (g/cm^3) = 1.19
Z = 8
Space group = P_{mmm}
Crystal system = Orthorhombic

Relative intensity	d_{obs}	d_{cal}	h	k	l
38	4.413	4.425	1	2	0
35	4.324	4.324	1	1	7
35	4.254	4.271	2	1	2
41	4.055	4.023	1	2	4
87	3.931	3.929	1	0	9
100	3.581	3.592	1	0	10
67	3.231	3.223	2	0	9
27	3.149	3.154	3	0	3
26	3.079	3.083	3	0	4
29	3.012	2.998	3	0	5
27	2.833	2.838	0	3	7
25	2.604	2.604	3	1	8
22	2.475	2.477	0	4	1
20	2.400	2.397	4	0	3
19	2.282	2.281	4	0	6
17	2.225	2.224	3	2	10

The lattice parameters along with 'd' values are summarised in Tables 2 and 3. The correctness of these values was confirmed by matching the observed density (D_{obs} = 1.19 g/cm^3 for nickel(II) complex and D_{obs} = 1.42 g/cm^3 for palladium(II) complex) with the calculated density (D_{cal} = 1.27 g/cm^3 for nickel(II) complex and D_{cal} = 1.52 g/cm^3 for palladium(II) complex) from the X-ray diffractograms. It may be concluded that nickel(II) and palladium(II) complexes are square-planar in structure and crystallise in orthorhombic system with space group P_{mmm} or P_{222}.[14]

TABLE-3

CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR $Pd(C_8H_8O_2N)_2$

a (Å) = 7.1049 ± 0.0083
b (Å) = 7.4420 ± 0.0084
c (Å) = 33.5890 ± 0.0607
α = 90°
β = 90°
γ = 90°

Volume (Å^3) = 1776.0410
D_{cal} (g/cm^3) = 1.52
D_{obs}(g/cm^3) = 1.42
Z = 4
Space group = P_{222}
Crystal system = Orthorhombic

Relative intensity	d_{obs}	d_{cal}	h	k	l
78	4.206	4.198	0	0	8
30	3.767	3.785	1	1	6
31	3.535	3.531	0	2	3
100	3.392	3.386	2	0	3
46	3.255	3.255	0	2	5
26	2.957	2.959	1	2	5
49	2.574	2.573	2	0	9
31	2.363	2.362	3	0	1
21	2.173	2.179	3	1	4
20	2.127	2.123	3	0	7
26	2.105	2.104	1	3	7
4	1.979	1.976	2	3	4
18	1.858	1.857	0	4	1

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