

## Short Communication

### Complexes of Cu (II), Ni (II) and Pd (II) with resacetophenone phenylhydrazone

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Received on September 6, 1981; Revised on May 15, 1982.

#### Abstract

The complexes of Cu (II), Ni (II) and Pd (II) with resacetophenone phenylhydrazone have been prepared and characterized by elemental analysis, magnetic measurements, infrared, electronic and ESR spectra, thermogravimetric curves, etc. Based on these data, the complexes are assigned square planar geometry.

Key words: Phenylhydrazone—Cu, Ni, Pd complexes, structural studies.

#### 1. Introduction

Hydrazones, characterized by the presence of triatomic grouping,  $\text{>C=N-N<}$  have been found to be of biological and analytical importance; they act as herbicides, insecticides, plasticizers, antioxidants, etc.<sup>1</sup>. Eight phenylhydrazones of *o*-hydroxyaldehydes and ketones have been synthesized by Raju *et al*<sup>2</sup> and among them resacetophenone phenylhydrazone has been used as gravimetric and amperometric reagent for copper<sup>3,4</sup> and *o*-hydroxyacetophenone phenylhydrazone as a gravimetric reagent for palladium<sup>5</sup>. In the present investigation, the complexes of Cu (II), Ni (II) and Pd (II) with resacetophenone phenylhydrazone (RPPH) have been prepared and characterised on the basis of physico-chemical data.

#### 2. Experimental

RPPH was prepared by the method reported in the literature<sup>6</sup>.

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The Cu (II) complex was prepared in sodium acetate medium by treating the solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (one mole) in water with RPPH (two moles) in methanol. Similarly, Ni (II) complex was prepared in ammoniacal medium and Pd (II) complex in 0.05 N HCl medium. The precipitate obtained, in each case, was digested on water bath, filtered and washed thoroughly with hot water and then with methanol until the washings were free from the reagent. The complexes were dried in vacuum over fused  $\text{CaCl}_2$ .

The elemental analyses (C, H, N) were obtained from Australian Microanalytical Service, Victoria, Australia. The ultraviolet and visible spectra in DMF were obtained on Toshniwal spectrophotometer (manual). The ESR spectra of the complexes in solid state were recorded at room temperature on Varian E-4 X-band spectrometer available at RSIC, IIT, Madras. The conductance measurements were made in 1,4-dioxan using Toshniwal type CL01/02 A conductivity bridge. The other data were obtained as described previously<sup>7</sup>.

### 3. Results and discussion

The analytical data presented in Table I indicate that the complexes of RPPH can be represented as  $\text{M}(\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$  where  $\text{M} = \text{Cu}, \text{Ni}$  or  $\text{Pd}$  and are brown yellow and green in colour respectively. The complexes are insoluble in water, dilute mineral acids and common organic solvents such as benzene, chloroform, nitrobenzene, carbontetrachloride, acetonitrile, etc. indicating that they are probably polymeric in nature. The polymeric form may be thought of being due to the formation of intermolecular hydrogen bonds by the free hydroxyl groups present. The complexes are, however, sparingly soluble in DMF and 1,4-dioxan. Because of their insolubility, their molecular weights could not be determined.

Table I

Elemental analysis of metal complexes of RPPH

Complex	Metal %	Carbon %	Hydrogen %	Nitrogen %
Cu $(\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$	11.37 (10.91)	57.86 (57.77)	4.87 (5.21)	9.71 (9.63)
Ni $(\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$	10.93 (10.17)	57.43 (58.25)	4.68 (5.25)	9.62 (9.71)
Pd $(\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$	17.96 (17.02)	54.12 (53.80)	4.50 (4.85)	9.10 (8.97)

Values in parentheses are the calculated ones,



Cu(II) complex is paramagnetic with an effective magnetic moment of 1.75 B.M. This is very close to the spin-only value (1.73 B.M.) with no orbital contribution expected, a case for square planar geometry by virtue of a non-degenerate ground state. The slight excess of magnetic moment over the spin-only value might, however, be due to spin-orbit coupling. Ni(II) and Pd(II) complexes are found to be diamagnetic.

The molar conductance of the complexes in 1,4-dioxan at the concentration  $10^{-3}$  M is too small to measure. The complexes are hence non-electrolytes in this solvent.

The thermograms of Cu(II), Ni(II) and Pd(II) complexes show weight loss in the temperature ranges 100–120° C, 60–120° C and 80–120° C respectively which, in each case, corresponds to the loss of two water molecules. The expulsion of water in the above ranges of temperature indicates that they are present outside the coordination sphere. The sharp decomposition associated with the loss of ligand starts at 192° C, 260° C and 280° C in the case of Cu(II), Ni(II) Pd(II), complexes respectively. The final products of decomposition of the complexes above 550° C correspond, in each case, to metallic oxide.

Some important infrared absorption frequencies are given in Table II.

The absorption peak at  $3310\text{ cm}^{-1}$  in RPPH is not sharp. Since both  $\nu\text{OH}$  and  $\nu\text{NH}$  absorptions fall almost in the same region<sup>8</sup>, they appear to have been merged. A band observed around  $1490\text{ cm}^{-1}$  in the ligand and the metal complexes has been assigned to  $\nu\text{C-N}$ <sup>9</sup>. The C=N stretching frequency occurring at  $1630\text{ cm}^{-1}$  in the ligand is lowered by  $80\text{--}100\text{ cm}^{-1}$  in the complexes suggesting that the nitrogen of azomethine group is coordinating<sup>10</sup>. A band at  $1235\text{ cm}^{-1}$  in the ligand assignable to phenolic  $\nu\text{C-O}$  undergoes a positive shift in the metal complexes. This may be ascribed to the drift of electron density from the oxygen atom to the metal ion resulting in greater ionic character of the C-O bond and a consequent increase in the C-O vibration frequency<sup>11</sup>. It would have been appropriate if the  $\nu\text{C-O}$  in the complexes were compared with  $\nu\text{C-O}$  in the potassium salt of the ligand. This, however, was not possible since the appropriate potassium salt could not be isolated. That the nitrogen of azomethine group and oxygen of *o*-hydroxy group are coordinating, is further evidenced by M-N and M-O bond frequencies (Table II).

The electronic spectrum of Cu(II) complex shows two peaks at  $16660\text{ cm}^{-1}$  and  $22725\text{ cm}^{-1}$  assignable to  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$  and  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  transitions respectively. The former transition is characteristic of square planar geometry<sup>12</sup>. Ni(II) complex gives a peak at  $21050\text{ cm}^{-1}$  and Pd(II) complex at  $14295\text{ cm}^{-1}$  both of which may be assigned to  ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$  transition<sup>13-15</sup>. Two peaks observed at  $33330\text{ cm}^{-1}$  and  $29410\text{ cm}^{-1}$  in the ligand as well as in complexes have been assumed to be due to intra-ligand transitions involving electron transfer.

The ESR spectrum of Cu(II) complex shows two somewhat broad peaks from which  $g_{\parallel}$  and  $g_{\perp}$  have been calculated to be 2.148 and 2.046 respectively. Orbital reduction parameters,  $K_{\parallel}^2$  and  $K_{\perp}^2$  have also been computed and found to be



Table II

IR absorption data (cm<sup>-1</sup>)

RPPH	Cu-complex	Ni-complex	Pd-complex	Assignment
3310	—	—	—	$\nu\text{N-H} + \nu\text{O-H}$
—	3410	3220	3386	$\nu\text{N-H}$
—	3300	3170	3270	Intermolecularly hydrogen bonded O-H
1490	1490	1490	1490	$\nu\text{C-N}$
1630	1550	1530	1530	$\nu\text{C=N}$
1235	1260	1250	1245	$\nu\text{C-O}$
—	485	490	480	$\nu\text{M-N}$
—	370	395	380	$\nu\text{M-O}$

0.3722 and 0.6314 respectively. Kivelson and Neiman<sup>16</sup> have shown that  $g_{\parallel}$  is the most sensitive function for indicating covalency. Normally  $g_{\parallel}$  is 2.3 or more for ionic environments and it is less than 2.3 for covalent environments. The value of  $g_{\parallel}$  obtained for Cu(II) complex is less than 2.3 indicating covalent character of metal-ligand bond in the complex. The observation that  $K_{\parallel}^2$  is less than  $K_{\perp}^1$  further indicates, as pointed out by Hathaway<sup>17</sup>, that the complex is in-plane  $\pi$ -bonded. The spectra of Ni(II) and Pd(II) complexes show no peak and hence they are confirmed to be diamagnetic in nature.

Based on the foregoing data, the complexes are assigned square planar geometry.

#### Acknowledgements

The authors thank Prof. G. Aravamudan, IIT, Madras, for the facilities offered for measuring magnetic susceptibility of the complexes.

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