

# Studies on the Mixed Ligand Complexes of Co(II), Ni(II) and Cu(II) with Phthalimide and Heterocyclic Amines

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**Abstract:** This paper describes the synthesis and characterization of mixed ligand complexes of Co(II), Ni(II) and Cu(II) with, Phthalimide and heterocyclic amines. The Elemental analysis, IR, UV-vis and <sup>1</sup>H-NMR spectral analysis, colours, molar conductances and magnetic properties suggested that the complexes have formulation as [M(Ph-imide)<sub>2</sub>(L)<sub>2-4</sub>], Where, M = Co(II), Ni(II) and Cu(II); Ph-imide = Phthalimide; L=Quinoline, Iso-quinoline, 2-Picoline and Pyridine. The prepared complexes of Co (II) and Ni (II) were octahedral and Cu (II) was square planar.

**Keywords:** Mixed Ligand Complex, Phthalimide, Heterocyclic Amines

## 1. Introduction

Organic compound containing imides group have both salt forming and coordinating properties. The resulting imide complexes are generally insoluble in polar solvents and soluble in non polar solvents and hence are very important from analytical point of view. Phthalimides possess a structural features –CO-N(R)-CO- and an imide ring which help them to be biologically active and pharmaceutically useful [1]. Phthalimides have received attention due to their antibacterial, antifungal, analgesic [2], antitumour [3, 4], anxiolytic [5] and anti HIV-1 activities. Scanty details on the studies of simple metal imide complexes are available in the literature but a very little work has been done on their mixed ligand complexes.

Recently, we studied few mixed ligand complexes containing heterocyclic amine as secondary ligands and few Schiff base containing complexes [6-15]. We report here, the synthesis and characterization of several new mixed ligand complexes of Co (II), Cu (II) and Ni (II) with Phthalimides as primary and heterocyclic amine bases as secondary ligands.

## 2. Experimental

### 2.1. Chemicals & Regents

All chemicals and reagents used were chemicals and reagents grades. The solvent were purified using the conventional methods.

### 2.2. Physical Measurements

Carbon, hydrogen and nitrogen analyses were carried out at the Liverpool University, Liverpool, England. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used for the magnetic moment measurement. Infrared spectra as KBr disc were recorded in a SHIMADZU FTIR-8400 (Japan) infrared spectrophotometer, from 4000-400 cm<sup>-1</sup>. The absorbance of the complexes were recorded on SHIMADZU Spectrophotometer (Model UV-1800. Metal was determined by weighing as the oxide produced by direct ignition. The proton NMR (<sup>1</sup>H) were carried out from the Liverpool University, Liverpool, England.

### 2.3. General Method for the Preparation of the Complexes of the Type [M(X)(L)]

$M^{2+} + X + L \rightarrow [M(X)(L)]$  Where, M = Co (II); Cu (II); Ni (II) ions,

X = Phthalimide and L= Heterocyclic amine bases such as Pyridine, Quinoline, Isoquinoline, 2-Aminopyridine, 2-Picoline.

An ethanolic solution (just dissolved) of M(II) chloride salts (2m mol) and ethanolic potassium hydroxide solution (just dissolved) of 'X' acid (4 m mol) were mixed and gently heating with stirring for half an hour. No precipitate was observed, and then secondary ligand in calculated ratio was added and stirring until complex precipitated. The precipitates were filtered, washed several times with alcohol and then dried in vacuum desiccator over phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>).

### 3. Results and Discussion

#### 3.1. Elemental Analysis and Conductivity Measurement

The analytical data and their physical properties of the complexes are tabulated in tables 1 and 2 respectively. The analytical data are in good agreement with the proposed empirical formulae of the prepared complexes. The molar conductances of 10<sup>-3</sup>M solution of the complexes in DMSO were measured at 30°C. The molar conductance values (Table 2), indicates that all the complexes are non-electrolytic in DMSO and proved that the anions are covalently bonded in all the cases.

#### 3.2. Magnetic Moment and Electronic Spectra

At room temperature magnetic susceptibility and electronic spectral components of the complexes are summarized in table 2 and 3. The Cu (II) complexes have  $\mu_{\text{eff}}$  values from 1.84 to 2.09 B.M corresponding to the presence of one unpaired electron. The reflectance spectra of Cu(II) complexes exhibit a broad band at 341 to 558 nm which is assigned to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  transition in a square-planar configuration [16] also the band observed at 398 to 502 nm may be assigned to charge transfer only. The magnetic moment value and the ligand field parameters confirmed all the Cu (II) complexes are square-planar configuration.

The Co (II) complexes possess magnetic moment in the range from 4.89 to 5.87 B.M. in agreement with the octahedral geometry [17]. The three transitions observed in the electronic spectra of the Co (II) complexes indicate the octahedral environment around the metal ion. The electronic spectra of the Co(II) complexes show strong peaks between 306 to 538nm assignable to the transitions  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ . The magnetic properties of high spin octahedral Co(II) complexes are governed by the orbit ally degenerate ground term  ${}^4T_{1g}$ ; this provides on orbital contribution to the magnetic moment. The electronic spectra of Ni (II) complexes showed peaks characteristic of octahedral geometry. The reflectance spectra of Ni (II) complex consist of the transition bands between 305 to 577 nm assignable to the transitions  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$

(F) respectively. The Ni (II) complexes possess magnetic moment in the range from 2.85 - 3.67 B.M in agreement with octahedral geometry [18].

#### 3.3. Infrared Spectral Spectra

Salient features of the IR spectra of the complexes are tabulated in the table 4. Imides ion that is the common constituent of all the complexes has two (NH and CO stretching) frequency regions. So it has also two (through O and N) coordination sites. The IR spectra can not make a sharp distinction whether coordination in through nitrogen or oxygen of the carbonyl group, because any change in the imides nitrogen which is directly linked to the carbonyl group will alter the molecular environment and hence the frequency of the latter even if it is not coordinated. However on the basis of Lewis acid concept it may be established that the negatively charged imides nitrogen will have possibilities of being coordinated than oxygen. Secondly, there will be steric hindrance if coordination is through oxygen [19]. There was a shifting in carbonyl stretching frequency from 1682 to 1624 cm<sup>-1</sup> in the spectra of complexes. This negative shift may be due to the mass effect [20]. The stretching frequency at 1370 cm<sup>-1</sup> due to  $\nu(C-N)$  in the spectra of imides also shifted to 1420 cm<sup>-1</sup> in the spectra of the complexes indicating thereby the coordination of the imides ion with the metal ion. The presence of metal nitrogen bonding in the complexes is evident from the appearance of  $\nu(M-N)$  modes at 412 to 490 cm<sup>-1</sup> in the spectra of the complexes.

#### 3.4. <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR spectra of the complex [Co (Ph-imide)<sub>2</sub>(Py)<sub>4</sub>] were recorded in DMSO-d<sub>6</sub> and CDCl<sub>3</sub> solution respectively at room temperature. [Co(Ph-imide)<sub>2</sub>(Py)<sub>4</sub>]: 9.54-9.12 (m, 8H, Ar-H), 8.33-8.27 (m, 4H, Ar-H), 7.46-7.30 (m, 8H, Ar-H), 7.10-7.08 (m, 4H, Ar-H), 6.93-6.89 (m, 4H, Ar-H).

For the ligand pyridine, the ortho hydrogen atom has appeared at 8.47 ppm values. But after complexation with Co (II) metal ion, the ortho hydrogen in pyridine has sharply changed their position and in the complex they are in the range 9.54-9.12 ppm. Obviously, after coordination with the metal ion these two protons in ortho position are largely suffering from deshielding effect. The same effect is also working for the two protons at ortho position in phthalimide ring. According to the peak height and integration values of the protons in complex molecule, it is clear that four pyridine and two phthalimide molecule have taken part in complexation with the metal ion. Again, we can say from the <sup>1</sup>H NMR spectra of the complex that all the protons are available, those were in the individual ligands except imides proton.

**Table 1.** Analytical data of Co (II), Cu (II) and Ni (II) complexes.

Complexes	Yield %	M %	C %	H %	N %
[Co(II)(Ph-imide) <sub>2</sub> (Q) <sub>4</sub> ]	76	12.04 (12.75)	64.35 (64.79)	7.03 (7.56)	14.32 (14.86)
[Co(II)(Ph-imide) <sub>2</sub> (Py) <sub>4</sub> ]	64	8.45 (8.98)	77.23 (77.87)	5.02 (5.56)	12.03 (12.56)
[Cu(II)(Ph-imide) <sub>2</sub> (IQ) <sub>2</sub> ]	56	9.05 (9.61)	60.34 (60.76)	6.04 (6.82)	14.46 (14.92)
[Cu(II)(Ph-imide) <sub>2</sub> (2-Pico) <sub>2</sub> ]	67	14.34 (14.93)	62.23 (62.76)	6.03 (7.67)	12.35 (12.96)
[Ni(II)(Ph-imide) <sub>2</sub> (Q) <sub>4</sub> ]	72	12.24 (12.78)	65.34 (65.97)	7.04 (7.73)	14.02 (14.68)
[Ni(II)(Ph-imide) <sub>2</sub> (Py) <sub>4</sub> ]	63	9.23 (9.75)	64.04 (64.24)	4.53 (4.59)	13.34 (13.57)

Ph-imide=Phthalimide, Q= Quinoline, IQ=Iso-quinoline, Py= Pyridine, 2-Pico= 2-Picoline.

**Table 2.** Physical properties of Co (II), Cu (II) and Ni (II) complexes.

Complexes	Colour	Melting point ( $\pm 0.52^\circ\text{C}$ )	Molar conductance $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$	Magnetic moment $\mu_{\text{eff}}$ (B.M.)
[Co(II)(Ph-imide) <sub>2</sub> (Q) <sub>4</sub> ]	Brown	176	2.34	5.23
[Co(II)(Ph-imide) <sub>2</sub> (Py) <sub>4</sub> ]	Ash	198	0.98	4.98
[Cu(II)(Ph-imide) <sub>2</sub> (IQ) <sub>2</sub> ]	Pasty	148	0.67	1.98
[Cu(II)(Ph-imide) <sub>2</sub> (2-Pico) <sub>2</sub> ]	Green	197	1.32	2.09
[Ni(II)(Ph-imide) <sub>2</sub> (Q) <sub>4</sub> ]	Green	235	1.52	3.54
[Ni(II)(Ph-imide) <sub>2</sub> (Py) <sub>4</sub> ]	Bluish green	167	0.54	3.67

Ph-imide=Phthalimide, Q= Quinoline, IQ=Iso-quinoline, Py= Pyridine, 2-Pico= 2-Picoline.

**Table 3.** Electronic spectral data of Co (II), Cu (II) and Ni (II) complexes.

Complexes	$\lambda(\text{nm})$
[Co(II)(Ph-imide) <sub>2</sub> (Q) <sub>4</sub> ]	306
[Co(II)(Ph-imide) <sub>2</sub> (Py) <sub>4</sub> ]	334
[Cu(II)(Ph-imide) <sub>2</sub> (IQ) <sub>2</sub> ]	360
[Cu(II)(Ph-imide) <sub>2</sub> (2-Pico) <sub>2</sub> ]	341
[Ni(II)(Ph-imide) <sub>2</sub> (Q) <sub>4</sub> ]	315
[Ni(II)(Ph-imide) <sub>2</sub> (Py) <sub>4</sub> ]	305

Ph-imide=Phthalimide, Q= Quinoline, IQ=Iso-quinoline, Py= Pyridine, 2-Pico= 2-Picoline.

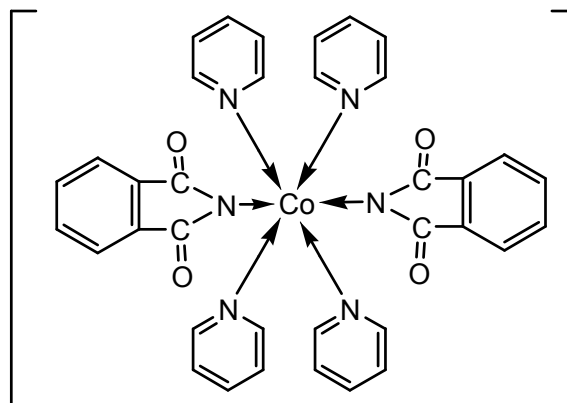
**Table 4.** IR spectral data of Co (II), Cu (II) and Ni (II) complexes.

Complexes	$\nu(\text{C=O}) \text{cm}^{-1}$	$\nu(\text{M-N}) \text{cm}^{-1}$	$\nu(\text{C-N}) \text{cm}^{-1}$	Aromatic Ring $\text{cm}^{-1}$
[Co(II)(Ph-imide) <sub>2</sub> (Q) <sub>4</sub> ]	1660	416	1390	750
[Co(II)(Ph-imide) <sub>2</sub> (Py) <sub>4</sub> ]	1630	470	1404	694
[Cu(II)(Ph-imide) <sub>2</sub> (IQ) <sub>2</sub> ]	1630	420	1350	730
[Cu(II)(Ph-imide) <sub>2</sub> (2-Pico) <sub>2</sub> ]	1677	490	1420	760
[Ni(II)(Ph-imide) <sub>2</sub> (Q) <sub>4</sub> ]	1624	445	1398	731
[Ni(II)(Ph-imide) <sub>2</sub> (Py) <sub>4</sub> ]	1682	414	1358	710

Ph-imide=Phthalimide, Q= Quinoline, IQ=Iso-quinoline, Py= Pyridine, 2-Pico= 2-Picoline.

## 4. Structure of the Complexes

IR spectra provide evidence that metal-imide bonding involves the nitrogen atom of the imide ring, the electronic spectra provide information on the nature of this bonding, <sup>1</sup>H NMR indicated that four pyridine and two Phthalimide taken part in complexation. On the basis of the elemental analysis, metal estimation, conductivity measurements, magnetic moment data, spectroscopic studies and literature review the structure of the complex 2 is assignable to have octahedral structure. The proposed structure of the complex 2 is shown below:

**Fig. 1.** Proposed structure of complex [Co(Ph-imide)<sub>2</sub>(Py)<sub>4</sub>].

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