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# SYNTHESIS AND X-RAY POWDER DIFFRACTION STUDIES: METAL COMPLEXES (Co(II), Ni(II) AND Cu(II)) OF SCHIFF BASE LIGAND 4-BROMO-2-CHLORO-6-[(1Z)-N-(PHENYL) ETHANIMIDOYL] PHENOL

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## ABSTRACT

***Schiff bases are an important class of organic compounds, which play an important role in medicinal and pharmaceutical applications. Co(II), Ni(II) and Cu(II) complexes with bidentate Schiff base ligand, 4-bromo-2-chloro-6-[(1Z)-N-(phenyl) ethanimidoyl] phenol (BCEP) have been successfully synthesized. The structural characterization of the synthesized metal complexes have been estimated by analyzing powder X-ray diffraction technique. It reveals that Co and Cu metal complexes crystallize in monoclinic system with P 1 $2_1$ 1 and P 1 $2_1$/a space group respectively, whereas Ni metal complex crystallizes in triclinic system with P$\bar{1}$space group.***

***Keywords: Schiff bases, metal complexes, powder X- ray diffraction study***

## INTRODUCTION

Schiff bases are condensation products of primary amines and carbonyl compounds and they discovered by a German chemist, Nobel Prize winner, Hugo Schiff in 1864. Structurally, Schiff base (also known as imine or azomethine) is an analogue of a ketone or aldehyde in which the carbonyl group (C=O) has been replaced by an imine or azomethine group. Schiff base ligands are essential in the field of coordination chemistry, especially in the development of complexes of Schiff bases because these compounds are potentially capable of forming stable complexes with metal ions[1]. The individual Schiff bases are considered to be promising antifungal medicines[2]. Isatin Schiff base ligands are marked by antiviral activity, and this fact is very useful in the treatment of HIV[3]. In addition, it is also found that these compounds have anticonvulsant activity and may be included in the anti-epileptic drugs[4]. Due to the presence of the imine group, the electron cloud of the aromatic ring and electronegative nitrogen, oxygen and sulfur atoms in the Schiff bases molecules, these compounds effectively prevent corrosion of mild steel, copper, aluminum and zinc in acidic medium[5]. Schiff bases and Mannich bases of isatin are known to possess a wide range of pharmacological properties including antibacterial, anticonvulsant, antifungal and antiviral activities[6-9]. Schiff's bases are also important compounds owing to their wide range of industrial applications[10]. As a part of our ongoing research on synthesis of novel compounds and characterization by X-ray diffraction studies[11-13], here we report the synthesis and characterizations of metal complexes (Co, Ni and Cu) of schiff base ligand 4-bromo-2-chloro-6-[(1Z)-N-(phenyl) ethanimidoyl] phenol.

## EXPERIMENTAL

### Synthesis: General Preparation of Metal chelates (Co(II), Ni(II) and Cu(II)) of Schiff base ligand 4-bromo-2-chloro-6-[(1Z)-N(phenyl) ethan imid oyl] phenol (BCEP)

The appropriate methanolic solution of transition metals (Co, Ni and Cu) (0.01mol, 10 ml) and schiff base ligand (BCEP) (0.02mol, 20 ml.) are taken in a 1:2 (metal/ligand) ratio. PH is maintained during the course of the reaction by adding few drops of liquid $N_2$. The reaction mass is refluxed for 3-4 hours on a water bath. After completion of the reaction, it is cooled to room temperature and solvent is evaporated naturally. Precipitated colored complex is filtered and washed with methanol: water (1:1) mixture, recrystallized from methanol and dried over anhydrous $CaCl_2$ in desiccators. It is further dried in an electric oven at 50-70 ℃. The chemical diagram of synthesized metal chelates (Co(II), Ni(II) and Cu(II)) of Schiff base ligand 4-bromo-2-chloro-6-[(1Z)-N-

(phenyl)ethanimidoyl] phenol (BCEP) are as shown in Figure 1a, 1b and 1c respectively.

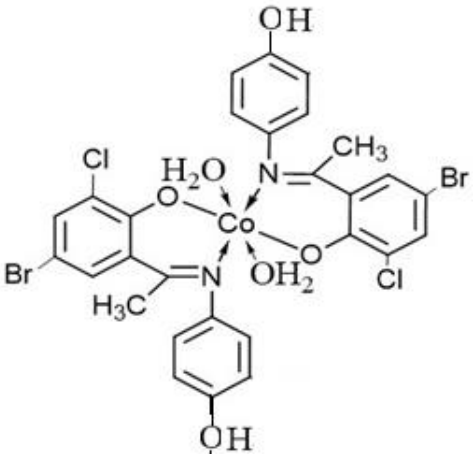


**Fig. 1(a)**

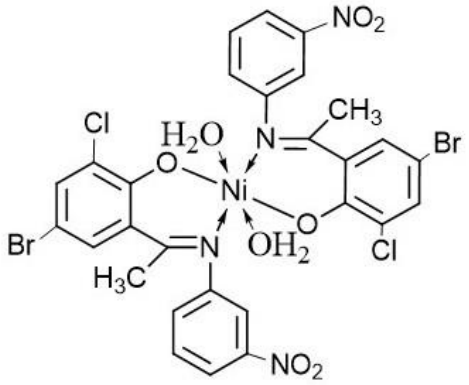


**Fig. 1(b)**

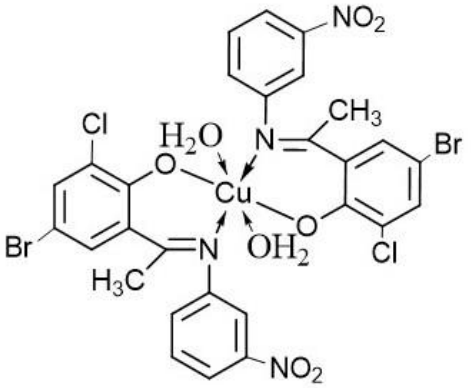


**Fig. 1(c)**

**Figure 1 The chemical diagram of metal chelates (Co(II), Ni(II) and Cu(II)) of Schiff base ligand 4-bromo-2-chloro-6-[(1Z)-N-(phenyl)ethanimidoyl] phenol (BCEP).**

## RESULTS AND DISCUSSION

Powder X- ray diffraction pattern are recorded for metal chelates (Co(II), Ni(II) and Cu(II)) of schiff base ligand 4-bromo-2-chloro-6-[(1Z)-N-(phenyl) ethanimidoyl] phenol (BCEP). All the diffraction data are collected on Rigaku Ultima IV diffractometer using CuKα1 radiation (λ = 1.5406 Å) and the powder diffraction patterns for all the metal complexes of Co, Ni and Cu are presented in the Figure 1a, 1b and 1c respectively. The Figure 1d shows the overlay diagram of powder XRD pattern of all three Co, Ni and Cu metal complexes. The experimental 2θ range is 05–60° with a step size of 0.01° and a counting time of 30 second per step. The program WinPLOTR package[14] are used for the graphics and all the experimental raw data are indexed by McMaille version 4.00 [15] method using DASH software package[16]. The figures of merit are achieved for Co metal complex are $F_{20}$ = 88.60 (0.0034, 68) and $M_{20}$ = 34.00. Pawley refinement results confirmed that Co metal complex is crystallizes in monoclinic system with space group P 1 $2_1$ 1 and unit-cell parameters: a = 19.9706 (0.0121) Å, b = 11.6535 (0.0080) Å, c = 10.9452 (0.0053) Å, α = 90°, β = 97.727 (0.031)°, γ = 90°, unit-cell volume V = 2524.125Å$^3$. In the metal complex of Ni, the figures of merit are as: $F_{20}$ = 84.76 (0.0074, 32) and $M_{20}$ = 27.84. The Ni complex crystallizes in triclinic system with space group $P\bar{1}$ and unit-cell parameters are, a = 11.0617 (0.0298) Å, b = 11.6582 (0.0269) Å, c = 14.4534 (0.0257) Å, α = 105.370 (0.127)°, β = 110.545 (0.113)°, γ = 109.779 (0.153)°, unit-cell volume V = 1478.394 Å$^3$. Indexing results of the third metal complex of Cu confirmed that it crystalizes in monoclinic with space group $P12_1/a$ and unit-cell parameters after the Pawley refinement are [a = 19.5983 (0.0120) Å, b = 14.4228 (0.0083) Å, c = 8.3842 (0.0041) Å, β = 92.106 (0.030)° and unit-cell volume V = 2368.306 Å$^3$]. The figures of merit obtained from the X-Ray data $F_{20}$ = 97.54 (0.0026, 80) and $M_{20}$ = 40.21.Table 1 summarized the significant peaks of 2θ, d-spacing, FWHM and corresponding (h k l ) for all three metal complexes of Co, Ni and Cu. The practical size of the synthesized compounds varies from 50 Å to 1000 Å for Co metal complex, 20 Å to 2000 Å for Ni metal complex and for Cu metal complex 100Å to 500Å respectively.

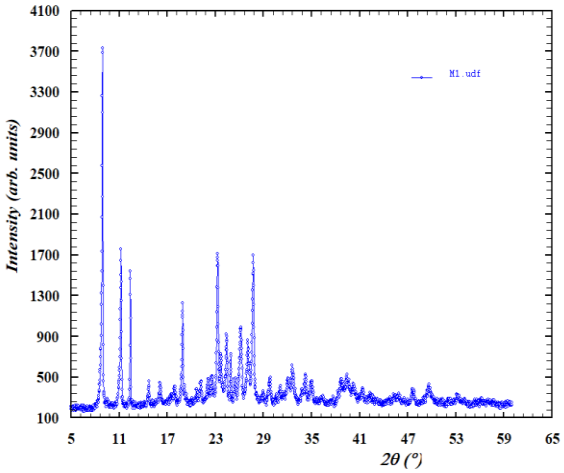


**Fig. 2 (a)**

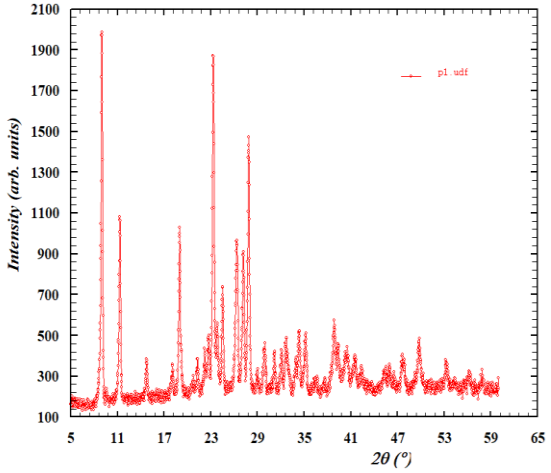


**Fig. 2 (b)**

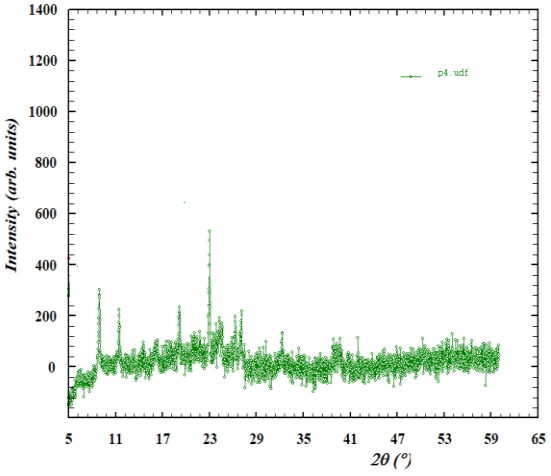


**Fig. 2 (c)**

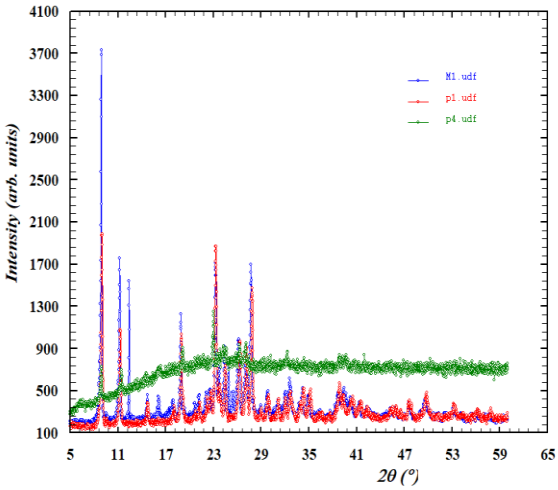


**Fig. 2 (d)**

**Figure 2 (a) XRD pattern of Co metal with ligand BCEP (b) XRD pattern of Ni metal with ligand BCEP and (c) XRD pattern of Cu metal with ligand BCEP (d) overlap diagram of XRD pattern of all three Co, Ni and Cu metal complexes; Color code: Blue- Co metal, Red –Cu metal and Green – Ni metal complexes.**

## CONCLUSION

A series of novel Co(II), Ni(II) and Cu(II) complexes with bidentate Schiff base ligand, 4-bromo-2-chloro-6-[(1Z)-N-(phenyl) ethanimido yl] phenol (BCEP) have been synthesized and characterized by powder X-ray diffraction technique. Powder X-ray diffraction graph shows that the synthesized metal complexes have been crystalline in nature and Co and Cu metal complex crystallizes in monoclinic system, whereas Ni metal complex crystallizes in triclinic system. The well-defined, sharp peaks in the XRD patterns signify the good crystalline and single phase nature of the pure.

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**Table-1 : X-ray powder diffraction data of all three metal complexes of Co, Ni and Cu; the significant peaks of 2θ, d-spacing, FWHM and corresponding hkl.**

| No. | 2-theta (deg) | d (ang.) | FWHM (deg) | (h k l ) |
|---|---|---|---|---|
| **For the Co metal complex** | | | | |
| 1 | 8.924(2) | 9.901(2) | 0.119(3) | (1 1 0) |
| 2 | 11.231(5) | 7.872(3) | 0.171(5) | (2 0 -1) |
| 3 | 12.374(4) | 7.147(2) | 0.070(3) | (1 1 1) |
| 4 | 14.748(5) | 6.001(2) | 0.169(17) | (3 0 -1) |
| 5 | 18.908(12) | 4.689(3) | 0.147(12) | (0 1 2) |
| 6 | 20.61(4) | 4.306(8) | 0.17(4) | (2 2 -1) |
| 7 | 21.226(14) | 4.182(3) | 0.213(19) | (2 1 2) |
| 8 | 22.09(3) | 4.022(5) | 0.42(7) | (3 2 -1) |
| 9 | 22.553(17) | 3.939(3) | 0.201(19) | (4 0 -2) |
| 10 | 23.282(5) | 3.8175(9) | 0.190(5) | (2 2 -2) |
| 11 | 23.685(11) | 3.7534(17) | 0.200(13) | (5 1 0) |
| 12 | 24.451(5) | 3.6376(8) | 0.198(7) | (1 0 -3) |
| **For the Ni metal complex** | | | | |
| 1 | 6.35(5) | 13.92(12) | 1.7(3) | (0 1 0) |
| 2 | 8.959(4) | 9.862(4) | 0.172(11) | (1 0 -3) |
| 3 | 11.46(2) | 7.714(14) | 0.125(17) | (1 -1 1) |
| 4 | 23.012(3) | 3.8616(5) | 0.038(7) | (2 -2 0) |
| **For the Cu metal complex** | | | | |
| 1 | 8.976(3) | 9.844(3) | 0.184(4) | (2 0 0) |
| 2 | 11.315(5) | 7.814(3) | 0.232(4) | (1 0 -1) |
| 3 | 18.12(3) | 4.891(9) | 0.25(3) | (4 0 0) |
| 4 | 19.006(5) | 4.6655(13) | 0.208(8) | (1 3 0) |
| 5 | 21.33(3) | 4.163(5) | 0.27(3) | (0 3 1) |
| 6 | 22.210(18) | 3.999(3) | 0.19(2) | (4 1 1) |
| 7 | 22.725(15) | 3.910(2) | 0.280(17) | (2 0 -2) |
| 8 | 23.280(4) | 3.8178(7) | 0.243(4) | (2 3 1) |
| 9 | 23.784(14) | 3.738(2) | 0.32(2) | (5 1 0) |
| 10 | 24.506(7) | 3.6296(10) | 0.221(7) | (0 2 2) |
| 11 | 26.359(7) | 3.3784(9) | 0.309(6) | (3 1 2) |