

# STUDIES ON METAL COMPLEXES WITH BENZO FURAN-2-CARBOXAMIDE AND BENZOTHIOPHENE-2-CARBOXAMIDE

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**Abstract**—Studies using benzo furan and benzothiophene derivatives are lacking. The donor ability of oxygen/sulphur atoms in these rings are generally poor owing to aromaticity, but complexes of their 2-carboxylic acids are known to involve both the heteroatom and the carboxyl group<sup>(1)</sup>. The purpose of this study was to prepare complexes with deprotonated and non-deprotonated benzo furan and benzothiophene-2-carboxamides to determine the nature of bonding, keeping in mid that the deprotonated carboxamides (like the deprotonated carboxylic acid) might was their heteroatom in bonding to metal ions. Unfortunately, however, the deprotonated complexes could not be prepared; the complexes prepared were only of protonated types.

## 1. INTRODUCTION

Various carboxamides of the N-heterocyclic ring system are known to give structurally important complexes through engagement of heteroatoms either alone or in conjunction with amide oxygen in non-deprotonated complexes or with amide nitrogen in deprotonated complexes<sup>(1-6)</sup>. However, references on similar studies using benzo furan and benzothiophene derivatives are lacking. The donor ability of oxygen/sulphur atoms .In these rings are generally poor owing to aromaticity, but complexes of their 2-carboxylic acids are known to involve both the heteroatom and the carboxyl group<sup>(7)</sup>. The purpose of this study was to prepare complexes with deprotonated and non-deprotonated benzo furan and benzothiophene-2-carboxamides to determine the nature of bonding, keeping in mid that the deprotonated carboxamides (like the deprotonated carboxylic acid) might was their heteroatom in bonding to metal ions. Unfortunately, however, the deprotonated complexes could not be prepared; the complexes prepared were only of protonated types (containing the ligands in their free forms).

The preparation and characterization of Cu(II), Ni(II) and Cu(II) complexes of benzo furan- and benzo

thiophene-2-carboxamides (Fig.1) on the basis of magnetic moments, conductance, electronic, infrared and esr spectral data. Bonding and stereochemistry of the complexes are also discussed.

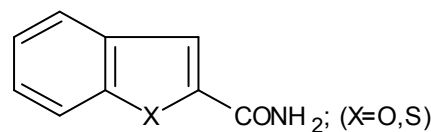


Fig. 1. Benzo Furan/Thiophene -2-Carboxamide

## 2. EXPERIMENTAL PROCEDURE

### 2.1 IR Spectra:

IR spectra were obtained using CsI discs in the range 4000–200 cm<sup>-1</sup> on a Perkin-Elmer 783 spectrophotometer.

### 2.2 Magnetic moments:

It was measured at room temperature.

### 2.3 Conductance measurement:

Conductivity measurements of the complexes were carried out mostly in dry nitromethane.

## 3. MATERIAL USED

Copper(II) chloride dehydrate, Benzo furan-2-carboxamide, nickel(II) chloride hexahydrate nickel(II) nitrate hexahydrate and Benzothiophene-2-carboxamide were purchased from Merck and B.D.H. (India) chemicals.

#### 4. SOLVENT USED

Absolute ethanol and tert-butyl alcohol were purified according to standard procedures.

#### 5. SYNTHESIS

Preparation of Complexes with (A) Benzo furan-2-carboxamide (BFuCA) and (B) Benzothiophene-2-carboxamide (BThCA):

##### [1] $\text{Cu}(\text{BFuCA})\text{Cl}_2 \cdot 1.5 \text{H}_2\text{O}$

A solution of 1.2 mmol of copper(II) chloride dihydrate dissolved in tert-butyl alcohol (10 ml) was added to a solution of 5 mmol of benzo furan-2-carboxamide in the same solvent. The mixed solution was concentrated on a steam bath and allowed to cool to room temperature. The compound deposited was filtered, washed with the same solvent and dried in a desiccators over fused  $\text{CaCl}_2$ .

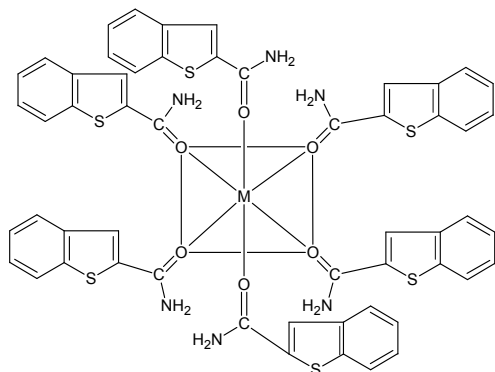


Fig. 2.  $[\text{M}(\text{BThCA})_6](\text{NO}_3)_2/(\text{ClO}_4)_2$ .  $\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II})$

##### [2] $\text{Ni}(\text{BFuCA})_4\text{Cl}_2$

A solution of 0.42 mmol of nickel(II) chloride hexahydrate dissolved in dry ethanol (10 ml) was added to a solution of 1.7 mmol of the ligand in the same solvent (10 ml). The mixed solution was refluxed, concentrated on a steam bath and allowed to cool to room temperature. The compound precipitated was filtered, washed with the same solvent and dried in a desiccator over fused  $\text{CaCl}_2$ .

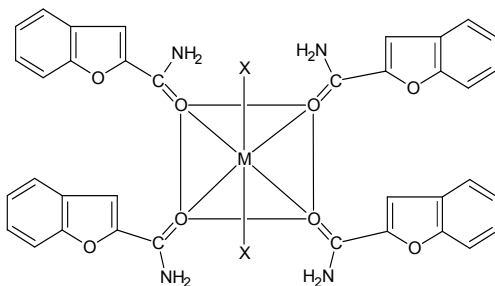


Fig. 3.  $[\text{M}(\text{BFuCA})_4\text{X}_2]$ ,  $\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II})$ ,  $\text{X} = \text{Cl}, \text{Br}$  &  $[\text{M}(\text{BFuCA})_4\text{X}_2](\text{NO}_3)_2/(\text{ClO}_4)_2$ ,  $\text{M} = \text{Ni}(\text{II}), \text{X} = \text{H}_2\text{O}$

##### [3] $\text{Cu}(\text{BThCA})\text{Cl}_2 \cdot \text{H}_2\text{O}$

0.6 mmol of copper(II) chloride dihydrate dissolved in tert-butyl alcohol (10ml) was added to a solution of 2.4 mmol of benzo thiophene-2-carboxamide (prepared according to literature using benzo ethyl thiophene-2-carboxylate) in the same solvent. The mixed solution was concentrated on a steam bath and allowed to cool to room temperature. The yellowish brown crystals which deposited were filtered, washed with the same solvent and dried in a desiccators over fused  $\text{CaCl}_2$ .

##### [4] $\text{Ni}(\text{BThCA})_4(\text{NO}_3)_2$

0.8 mmol of nickel(II) nitrate dissolved in tert-butyl alcohol (10ml) was added to a solution of 3.2 mmol of the ligand in same solvent (10ml). The mixed solution was concentrated on a steam bath, cooled, and to the cold concentrated solution solvent ether was added where upon the green compound precipitated. It was filtered, washed with tert-butyl alcohol and dried in a desiccators over fused  $\text{CaCl}_2$ .

#### 6. RESULTS AND DISCUSSION

##### (i) Magnetic Moments Studies:

The room temperature magnetic moments (Table 7.1) of the copper complexes occur in the normal range (1.75–2.20 B.M.) for square planar or octahedral structures without interactions between copper atoms. The values for the cobalt and nickel complexes lie in the expected range [4.7–5.2 B.M. for cobalt(II) and 2.9–3.4 B.M. for nickel(II)] for octahedral stereochemistry<sup>(8)</sup>.

##### (ii) Conductance Measurements:

Conductivity measurements (Table 7.1) of the complexes were carried out mostly in dry nitromethane. Because of solubility limitations, however, the measurements for the BFuCA complexes of nickel(II) chloride and nickel(II) bromide were made in ethanol and acetonitrile, respectively. The  $\Lambda_M$  values are low, being below the range<sup>(9)</sup> for uni-univalent electrolytes for all but the complexes of metal perchlorates the latter are uni-bivalent electrolytes. Coordination of anions (except the perchlorates) is, therefore, suggested.

##### (iii) Infrared Spectral Studies

###### a) Benzo Furan-2-Carboxamide

IR spectra (Table 3,4) recorded in CsI discs in the range 4000–200  $\text{cm}^{-1}$  indicate bands at 1662 and at 3180  $\text{cm}^{-1}$  assigned to  $\nu_{\text{C}=\text{O}}$  and to  $\nu_{\text{N}-\text{H}}$  and  $\nu_{\text{as}} \text{NH}_2$  modes, respectively<sup>(10,11)</sup>. In all but the complexes of copper(II) the  $\nu_{\text{s}} \text{OCN}$  and  $\nu_{\text{as}} \text{OCN}$  are shifted to higher and lower wave numbers, respectively, indicating coordination by the oxygen atom of the amide group<sup>(12)</sup>. In the copper complexes practically no shifts occur, implying little participation of the amide group in coordination.

In all the complexes, the C–O–C stretching frequency of the benzo furan ring in the ligand remains almost unaltered in position in the complexes, showing non-participation of the benzo furan ring oxygen in coordination.<sup>(13)</sup>

For the copper complexes it thus appears that the ligand is either very weakly coordinated or only incorporated in the crystal lattice of the host metal salt<sup>(14)</sup> and for others the ligand is bonded through the amide oxygen only.

The complexes of cobalt(II) and nickel(II) perchlorates show the characteristic strong broad band at  $\sim 1100\text{ cm}^{-1}$  along with others  $\sim 925\text{--}930$  and  $625\text{--}630\text{ cm}^{-1}$  with very weak splitting, indicating that the perchlorates are ionic. For the nitrate complexes, the characteristic bands at  $\sim 1370$  and  $830\text{--}840\text{ cm}^{-1}$  do not suggest coordination of the nitrate group. (Table 1)

In contrast to the cobalt(II) complexes, the complexes of nickel(II) nitrate and perchlorate all have bands at  $\sim 3000\text{--}3300\text{ cm}^{-1}$  merged into one broad contour due to the presence of water, presumably coordinated, to give six coordination around the metal ion. (Table 4)

**Table 1: Infrared Spectra of Benzo Furan-2-carboxamide (BFuCA), Benzo Thiophene-2-carboxamide (BThCA) and their Metal Complexes, Tentative Assignments,  $\text{cm}^{-1}$**

S. No.	Ligand/Complex	$\nu\text{NH}_2$	$\nu\text{C=O}$	$\delta\text{NH}_2$	$\nu\text{C-N}$
1.	BFuCA	3190(m,sp), 3350(m,sp)	1662(s)	1625(m,s p)	1410(s)
2.	$\text{Cu}(\text{BFuCA})\text{Cl}_2 \cdot 5\text{H}_2\text{O}$	3160(m,sp), 3350(m,sp)	1662(s)	1623(m,s p)	1410(s)
3.	$\text{Cu}(\text{BFuCA})_4(\text{NO}_3)_2$	3180(m,s), 3330(m,sp)	1660(s)	1615(m,s p)	1402(w,s p)
4.	$\text{Cu}(\text{BFuCA})_4(\text{ClO}_4)_2$	3180(m,sp), 3340(m,sp)	1655(s)	1620(sh)	1405(s)
5.	$\text{Ni}(\text{BFuCA})_4\text{Cl}_2$	3180(m,sp),3200(m,sp), 3305(m,sp)	1660(s)	1440(s)	
6.	$\text{Ni}(\text{BFuCA})_4\text{Br}_2$	3200(m,sp), 3325(m,sp)	1645(s)	1590(m,s p)	1435(s)
7.	$\text{Ni}(\text{BFuCA})_4(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	ca.3200(br, envelope)	1638(s)	1590(sh)	1430(sh)
8.	$\text{Ni}(\text{BFuCA})_4(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	ca.3300 (br, envelope)	1645(s)	1600(m,s p)	1438(s,sp)

#### (iv) Thermogravimetric Analysis

The data indicate the low thermal stability of the complexes. In some cases total loss of the organic ligand occurs in one step (e.g., benzo furan-2-carboxamide-CuCl<sub>2</sub> complexes). In some others (e.g., Benzo thiophene-2-carboxamide-Cu(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub> and benzo furan-2-carboxamide-Ni(NO<sub>3</sub>)<sub>2</sub> complexes) continuous loss

is found to take place until the end products are attained. The complexes The data indicate the low thermal stability of the complexes. The curves show that in some cases total loss of the organic ligand occurs in one step (e.g., benzo furan-2-carboxamide-CuCl<sub>2</sub> complexes). (Table 2)

**Table 2: Termogravimetric Analysis of the Complexes of Benzo Furan-2-carboxamide (BFuCA) and Benzo Thiophene-2-carboxamide (BThCA)**

#### Thiophene-2-carboxamide (BThCA)

S. No.	Complexes	% loss found (calc.) at temperature ranges			
		(A) 30–120°	(B) 120–210 /220°	(C) 230/240– 290°	(D) 30–370°
1.	$\text{Cu}(\text{BFuCA})\text{Cl}_2 \cdot 5\text{H}_2\text{O}$	10.0 (9.9)	44.0 (45.2)	–	–
2.	$\text{M}(\text{BFuCA})_4\text{Cl}_2$ (M = Ni, Co)	0	65.0 (58.8)	42.3 (46.0)	**80.0 (77.4) *85.0 (86.0)
3.	$\text{M}(\text{BFuCA})_4\text{Br}_2$ (M = Ni, Co)	0	68.0 (67.0)	0	**72.5 (67.0) *87.5 (87.9)
4.	$\text{Cu}(\text{BFuCA})_4(\text{NO}_3)_2$	0	76.0 (70.3) <sup>1</sup>	49.0 (57.6) <sup>2</sup>	91.0 (87.4)
5.	$\text{M}(\text{BFuCA})_4(\text{NO}_3)_2 \cdot \text{XH}_2\text{O}^a$ M = Ni, X = 2; Co, X=O	–	–	–	**90.0 (88.7) *93.0 (90.9)

#### 7. CHARACTERIZATION

The spectra of the complexes of nickel(II) with both benzo furan and benzo thiophene-2-carboxamides in the solid state as well as in solution exhibit bands whose positions and intensity suggest octahedral stereochemistry.

In the solid state, the likely nickel(II) nitrate/perchlorate-BFuCA complexes are  $[\text{Ni}(\text{BFuCA})_4(\text{H}_2\text{O})_2](\text{NO}_3)_2/(\text{ClO}_4)_2$  (Fig.6), and the corresponding BThCA complexes are  $[\text{Ni}(\text{BThCA})_6][\text{NO}_3)_2/(\text{ClO}_4)_2$  (Fig. 5). The presence of ionic anions and coordinated water is evident from their infrared spectra. In solution in nitromethane, the conductance data for their complexes suggest ionic perchlorates and covalently bonded nitrates:  $[\text{Ni}(\text{BThCA})_4(\text{NO}_3)_2]$ ,  $[\text{Ni}(\text{BThCA})_6](\text{ClO}_4)_2$ ,  $[\text{Ni}(\text{BFuCA})_4(\text{NO}_3)_2]$ ,  $[\text{Ni}(\text{BFuCA})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ . The absorbing species for the octahedral  $\text{NiX}_2\text{-BFuCA}$  (X=halogen) complexes in both phases is probably  $[\text{Ni}(\text{BFuCA})_4\text{X}_2]$  (Fig. 6), although in solution occurrence of species resulting from displacement of coordinated halide ions by the solvent cannot be discounted, considering conductance data.(Table 3)

**Table 3: Analyses, Colour, Magnetic Moments and Conductance Values of the Complexes of Benzo Furan–2–carboxamide (BFuCA) and BenzoThiophene–2– carboxamide (BThCA)**

S. No.	Complexes	Colour	Approx. yield (%)	Magnetic moment $\mu_{\text{eff}}$ (BM) at 27°C	Conductance* (Nitromethane)
1	Cu(BFuCA) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	Blue green	50	1.88	25.52
2.	Cu(BFuCA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Green	50	1.98	225.6
3.	Ni(BThCA) <sub>6</sub> (NO <sub>3</sub> ) <sub>2</sub>	Green	40	3.12	12.41
4.	Ni(BThCA) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Green	40	3.04	145.0
5.	#Co(BThCA) <sub>6</sub> (NO <sub>3</sub> ) <sub>2</sub>	Pink	40	5.12	21.68
6.	Co(BThCA) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Pink	40	5.01	146.4
7.	Cu(BThCA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Green	50	1.89	142.9
8.	Cu(BThCA) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	Green	50	1.85	10.59
9.	Cu(BThCA)Cl <sub>2</sub> .H <sub>2</sub> O	Yellow Brown	70	1.99	4.74

BThCA-(C<sub>9</sub>H<sub>7</sub>NOS)

**Table 4: Infrared Spectra of Benzo Furan–2–carboxamide (BFuCA), Benzo Thiophene–2–carboxamide (BThCA) and their Metal Complexes,**

S. No.	Ligand/Complex	$\nu_{\text{NH}_2}$	$\nu_{\text{C=O}}$	$\delta_{\text{NH}_2}$	$\nu_{\text{C-N}}$
1.	Co(BFuCA) <sub>4</sub> Cl <sub>2</sub>	3180(m,sp), 3310(m,sp)	1660(s)	1598(m,sp)	1455(s)
2.	Co(BFuCA) <sub>4</sub> Br <sub>2</sub>	3200(m,sp), 3310(m,sp)	1645(s)	1590(m,sp)	1435(s)
3.	Co(BFuCA) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	3200(m,sp), 3330(m,sp)	1640(s)	1390(w,sp)	1435(m,sp)
4.	Co(BFuCA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	3205(m,sp), 3330(m,sp)	1642(s)	1590(m,sp)	1438(s,sp)
5.	BThCA	3170(s), 3360(s)	1650(s)	1603(s)	1428(s)
6.	Cu(BThCA)Cl <sub>2</sub> .H <sub>2</sub> O	3310(s), 3220(w), 3400(sh), 3170(m,br)	1625(s)	–	1440(s)
7.	Cu(BThCA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	3430(sh), 3395(m), 3330(m), 3290(w,sh), 3250(m,sp), 3170(br,sh), 3100(sh),3080(sh)	1634(s)	–	1450(s)

8.	Ni(BThCA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	3400(s), 3330(m,s), 3305(w), 3250(m,s),3200(w),3105(m,sp) 3085(w)	1635(s)	–	1450(s)
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## 8. CONCLUSION

The copper(II) chloride complex appears orthorhombic, similar to the corresponding benzo thiophene–2–carboxamide compound. The copper(II) nitrate benzo–furan–2–carboxamide complex is of reversed axial type with  $g_{\parallel} < g_{\perp}$ , suggesting a  $d_z^2$  ground state. However, it has been reported that reversed ESR spectrum of a Cu(II) powder can occur for a  $d_{x^2-y^2}$  rather than a  $d_z^2$  ground state if there are non–equivalent sites within the unit cell<sup>(14–15)</sup>. The spectrum of the Cu(ClO<sub>4</sub>)<sub>2</sub> benzo furan–2–carboxamide complex is axial, with copper hyperfine lines in the parallel region that are not resolved.

The complexes of cobalt(II) and nickel(II) chloride with benzo furan–2–carboxamide, however, lose ligands in two distinct stages. Monovalent copper; benzo thiophene–2–carboxamide was evidently strongly reducing at high temperature.

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