www.vbripress.com, www.amlett.com, DOI: <u>10.5185/amlett.2011.9307</u>

Published online by the VBRI press in 2012

# Microwave induced synthesis and characterization of semiconducting 2thiophenecarboxaldehyde metal complexes

# A. P. Mishra<sup>\*</sup>, A. Tiwari, Rajendra K. Jain

Synthetic Inorganic & Coordination Chemistry Laboratories Department of Chemistry, Dr. H.S. Gour Central University, Sagar (M.P.) 470003, India

\*Corresponding author. Tel: (+91) 9981857386; E-mail: apm19@rediffmail.com and jainrajchem@gmail.com

Received: 25 September 2011, Revised: 08 December 2011 and Accepted: 15 January 2012

## ABSTRACT

The coordination complexes of Co(II), Ni(II) and Cu(II) derived from 2-thiophenecarboxylidene-3-chloro-4-fluoroaniline (TCC) and 2-thiophenecarboxylidene-4-fluoroaniline (TCF) have been synthesized by conventional as well as microwave methods. These compounds have been characterized by elemental analysis, FT-IR, FAB-mass, molar conductance, electronic spectra, ESR, thermal, magnetic susceptibility, electrical conductivity and XRD analysis. The complexes are coloured and stable in air. Analytical data revealed that all the complexes exhibited 1:2 (metal:ligand) ratio with the coordination 4 or 6. FAB-mass and thermal data show degradation pattern of the complexes. The thermal behavior of metal complexes shows that the hydrated complexes loses water molecules of hydration in the first step; followed by decomposition of ligand molecules in the subsequent steps. The crystal system, lattice parameter, unit cell volume and number of molecules in unit cell in the lattice of complexes have been determined by XRD analysis. XRD patterns indicate crystalline nature for the complexes. The solid state electrical conductivity of the metal complexes has also been measured. Solid state electrical conductivity studies reflect semiconducting nature of the complexes.

Keywords: Microwave synthesis; 2-thiophenecarboxaldehyde; thermal analyses; electrical conductivity; XRD.



**A.P. Mishra** is a professor of inorganic chemistry in Dr. H.S. Gour Central University, Sagar (M.P.). He has received the D.Phil. degree in 1984 and D.Sc. degree in 2004 from Allahabad University, India. His main research interest is advanced solid materials, nanoprecursor materials and bioinorganic chemistry. He has published many research papers in various national and internationally reputed journals.



Annapoorna Tiwari received the Ph.D. degree from Dr. H.S. Gour Central University, Sagar (M.P.) India. Her main research interest is inorganic materials.



**Rajendra K. Jain** received the Ph.D. degree from Dr. H.S. Gour Central University, Sagar (M.P.) India. His main research interest is materials science and green chemistry.

## Introduction

Metal complexes have been receiving considerable attention for many years, due to their interesting characteristics in the field of material science and biological systems. Optoelectronic, electrical and magnetic properties of the metals and metalloids can be tailored by reacting them with different ligands. A large number of Schiff bases and their complexes may exhibit the properties like- to reversibly bind oxygen, transfer of an amino group, as nanoprecursors and varied complexing/redox ability. The Schiff bases have high affinity to chelate with the transition metal ions, hence are attracting attention due to potential applications in areas viz. biology, catalysis, thermal, electrical, optical , magnetic etc [1-4]. A Transition metal complexes which usually contain nitrogen, sulphur/or oxygen as ligand atoms are becoming increasingly important because these Schiff base can bind with different metal centers involving various coordination sites and allow successful synthesis of metallic complexes with interesting stereochemistry. Heterocyclic compounds are widely distributed in the nature and essential to many biochemicals, analytical and industrial processes. Compounds containing these heterocycles have important properties in the field of material science and biological systems [5-8].



Fig. 1. Synthesis of Schiff base ligands

Microwave-assisted synthesis is a branch of green chemistry. The application of microwave-assisted synthesis in organic, organometallic and coordination chemistry continues to develop at an astonishing pace. Microwave irradiated reactions under solvent free or less solvent conditions are attractive offering reduced pollution, low cost and offer high yields together with simplicity in processing and handling. The salient features of microwave approach are shorter reaction times, simple reaction conditions and enhancements in yields [9-13]. Reports on the synthesis of metal complexes by microwave methods have been comparatively less.

In this study we report the synthesis and physicochemical characterization of Co(II), Ni(II) and Cu(II) complexes with ligands derived from 2-thiophenecarboxylidene-3-chloro-4-fluoroaniline (TCC) and 2-thiophenecarboxylidene-4-fluoroaniline (TCF) (Fig. 1). Some of the findings relating to structural and biological studies as a part of this paper have been published elsewhere [14]. The metal complexes formed with these two new ligands may be used as precursors for the synthesis of new compounds. Some of which them may exhibit interesting physical and chemical properties.

## Experimental

All the reagents used for the preparation of the Schiff bases were obtained from Sigma Aldrich (purity 97-99%). Metal salts were purchased from Loba Chemie. Elemental analyses were performed on an Elemental Vario EL III Carlo Erba 1108 analyzer. FAB-mass spectra were recorded on a JEOL SX 102/DA 6000 Mass Spectrometer using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. Electronic spectra (in DMSO) were recorded on Perkin Elmer Lambda-2Bspectrophotometer. Molar conductance measurements were conducted using 10<sup>-3</sup> M solutions of the complexes in DMSO on Elico-CM 82 Conductivity Bridge at room temperature. Magnetic susceptibility measurements were carried out on a Gouy balance at room temperature using CuSO<sub>4</sub>.5H<sub>2</sub>O as the calibrant. FT-IR spectra were recorded in KBr medium on a Perkin Elmer RX1 spectrophotometer in wave number region 4000-400 cm<sup>-1</sup>. X-band EPR spectra were recorded on a Varian E-112 spectrometer at room temperature operating at the X-band region with 100 kHz modulation frequency, 5 mw microwave power and 1 G modulation amplitude using TCNE as the internal standard. Thermogravimetric analysis was carried out under atmospheric condition with a heating rate 10°C min<sup>-1</sup> on TGA Q500 universal V4.5A TA instrument. Powder X-ray diffraction (XRD) patterns were recorded on a RINT2000 wide angle goniometer. X-ray diffractometer, operated at 40 kV and 30 mA generator using the CuKa line at 1.54056 Å as the radiation sources. Sample was scanned between 5° to  $70^{\circ}$  (2 $\theta$ ) at 25 °C. The solid state electrical conductivity has been measured by impedance spectroscopic method using HIOKI 3532-50 LCR Hitester at fixed frequency 1 KHz in the temperature range of 298-413 K. Microwave assisted synthesis were carried out in open glass vessel on a modified microwave oven model 2001 ETB with rotating tray and a power source 230 V, microwave energy output 800W and microwave frequency 2450 MHz. A thermocouple device was used to monitor the temperature inside the vessel of the microwave. The microwave reactions were performed using on/off cycling to control the temperature.

## Conventional method for the Synthesis of Schiff bases

TCC and TCF Schiff bases were synthesized by the condensation of equimolar ratio of 2thiophenecarboxaldehyde and 3-chloro-4-fluoroaniline with 4-fluoroaniline dissolved in ethanol. The resulting reaction mixture was stirred well, refluxed for 4-6 h and then allowed to cool overnight. The coloured solid precipitate of Schiff base obtained was filtered, washed with cold ethanol several times and dried in air at room temperature and finally stored under reduced pressure in a CaCl<sub>2</sub> desiccator. The purity of synthesized compounds was checked by TLC using silica gel G (yield: TCC = 78.1%; TCF = 80.0%).

## Microwave method for the Synthesis of Schiff bases

The equimolar (1:1) ratio of 2-thiophenecarboxaldehyde and 3-chloro-4-fluoroaniline with 4-fluoroaniline were mixed thoroughly in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-4 mL of dry ethanol as a solvent. The reaction was completed in a short time (3-4 min) with higher yields. The resulting product was then recrystallized with ethanol, finally dried under reduced pressure over anhydrous CaCl<sub>2</sub> in a desiccator. The progress of the reaction, purity of the product was monitored by TLC using silica gel G (yield: TCC = 88.4%; TCF = 90.0%). The applications of microwave irradiation are used for carrying out chemical transformations, which are pollution free, eco-friendly, low cost and offer high yields together with simplicity in processing and handling.

## Conventional method for the Synthesis of metal complexes

The metal complexes were prepared by the mixing of (50 mL) ethanolic solution of  $CoCl_2.6H_2O/NiCl_2.6H_2O/CuCl_2.2H_2O$  with the (50 mL) ethanolic solution of Schiff bases (TCC/TCF) in 1:2 (metal:ligand) ratio. The resulting mixture was refluxed on water bath for 5-8 h. A coloured product appeared on standing and cooling the above solution. The precipitated complex was, filtered washed with ether and recrystallized with ethanol several times and dried under the reduced pressure over anhydrous CaCl<sub>2</sub> in a desiccator. It was further dried in electric oven at 50-70 °C (yield: 63-72%).

## Microwave method for the Synthesis of metal complexes

The ligand and the metal salts were mixed in 1:2 (metal:ligand) ratio in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-5 mL of dry ethanol as a solvent. The reaction was completed in a short time (6-8 min) with higher yields. The resulting

## **Results and discussion**

As a result of microwave assisted synthesis, it was observed that the reaction was completed in a short time with higher yields compared to the conventional method. In the microwave method homogeneity of reaction mixture was increased by the rotating of reaction platform tray. The confirming of the results was also checked by the repeating of the synthesis process.

All the metal complexes are coloured, solid and stable towards air and moisture at room temperature. They decompose on heating at high temperature and more or less soluble in common organic solvents. The comparison study data of microwave and conventional methods, with analytical and physical data of the compounds are given in the **Table 1**. All the metal chelates have 1:2 (metal:ligand) stoichiometry. The molar conductance in DMSO of the complexes are 129.2, 49.5 and 56.2 Scm<sup>2</sup>mol<sup>-1</sup> respectively, for Co(II), Ni(II) and Cu(II) complexes of TCC. This indicates the Co(II) complex is electrolytic nature while Ni(II) and Cu(II) complexes are non-electrolytic nature. The molar conductance values for Co(II), Ni(II) and Cu(II) complexes of TCF are 120.1, 39.6 and 46.5 Scm<sup>2</sup>mol<sup>-1</sup> respectively. This indicates the nature of Co(II) as electrolytic and Ni(II) and Cu(II) complex are nonelectrolytic.

Fable 1. The c	comparative re-	sults of	conventiona	l and mic	rowave
nethods, analytic	al, physical da	ta and n	nagnetic mon	nent values	s of the
compounds.					

	Reaction period		Yield (%)		Eleme	Elemental Analysis Found/Calcd. (%)			
Molcular formula/ Mol. Wt./(Colour)	CM (h.)	MM (min.)	СМ	ММ	С	н	N	М	*14
C <sub>11</sub> H <sub>7</sub> NCIFS [TCC] 240 (Light Yellow)	3.2	4.9	78.1	88.4	54.54 (55.00)	2.89 (2.91)	5.78 (5.83)	-	
[Co(C <sub>11</sub> H <sub>7</sub> NCIFS) <sub>2</sub> ]Cl <sub>2</sub> .3H <sub>2</sub> O 664 (Bitter almond)	8.0	7.4	65.0	81.5	39.81 (39.75)	3.01 (3.01)	4.02 (4.21)	8.88 (8.87)	129
[Ni(C <sub>11</sub> H <sub>7</sub> NCIFS) <sub>2</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O 646 (Green)	6.8	6.8	63.0	84.3	40.74 (40.86)	3.04 (3.09)	4.32 (433)	9.03 (9.06)	49.
[Cu(C <sub>11</sub> H <sub>7</sub> NCIFS) <sub>2</sub> Cl <sub>2</sub> ] 614 (Black)	6.3	6.1	68.0	83.5	42.64 (42.99)	2.26 (2.28)	4.52 (4.56)	10.26 (10.34)	56.
(C <sub>11</sub> H <sub>8</sub> NFS) [TCF] 205 (Black)	4.1	5.0	80.0	90.0	64.39 (64.42)	3.90 (3.95)	6.82 (6.88)		
[Co(C <sub>11</sub> H <sub>8</sub> NFS) <sub>2</sub> ]Cl <sub>2</sub> .2H <sub>2</sub> O 576 (Green)	7.9	8.1	68.0	81.2	45.83 (45.75)	3.47 (3.46)	4.86 (4.85)	10.23 (10.21)	120
[Ni(C <sub>11</sub> H <sub>8</sub> NFS) <sub>2</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O 576 (Green)	7.6	7.2	72.0	85.1	45.83 (45.75)	3.47 (3.46)	10.16 (10.14)	10.16 (10.14)	39.
[Cu(C <sub>11</sub> H <sub>8</sub> NFS) <sub>2</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O 580 (Black)	7.2	7.0	70.0	81.6	45.50 (45.52)	3.41 (3.45)	4.79 (4.81)	6.22 (6.29)	46.

\*Conductance  $(\Lambda_m) = \text{Scm}^2 \text{mol}^{-1}$ 

CM = conventional method and MM = microwave method

#### FAB-mass spectrum

The FAB-mass spectra suggested that all the complexes have a monomeric nature. These complexes show molecular ion peaks in good agreement with the empirical formula suggested by elemental analyses. The FAB mass spectrum gives additional information about the analyzed species. The FAB mass spectra of [Ni(TCC)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O (Fig. 2) shows a molecular ion peak ( $M^+$ ) at m/z, 648 confirm the proposed formula. The spectrum of complex also shows a series of peak 611, 543, 470, 375, 278 and 107 corresponding to various fragments. Their intensity gives an idea of stability of the fragments. The value of 105 corresponds to Ni metal with N donor S as ligand moiety. The FAB mass spectrum gives additional structural information about the analyzed species. The FAB mass spectrum of [Cu(TCF)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O complex shows a molecular ion peak (M<sup>+</sup>) m/z =580 amu, which suggest the monomeric nature of the complex. The spectrum of the complex also shows a series of peaks corresponding to various fragments 541, 469, 434, 354, 280 and 107. Their intensity gives an idea about stability of the fragments [15, 16].



**Fig. 2.** FAB-mass spectrum of [Ni(TCC)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O complex

#### IR spectra

The data of the IR spectra of Schiff base ligand and its metal complexes are listed in **Table 2.** The IR spectra of the complexes were compared with those of the free ligand in order to determine the involvement of coordination sites in chelation. Characteristic peaks in the spectra of the ligand and complexes were considered and compared. The IR spectra of TCC ligand (**Fig. 3**) exhibits a strong band at 1630 cm<sup>-1</sup> due to v(C=N) azomethine group. This band shifts to lower energy region by 20-27 cm<sup>-1</sup> in the complexes. It suggests bonding through azomethine nitrogen. A strong band was observed at 848 cm<sup>-1</sup>, assignable to v(C-S-C) of thiophene. The band position of v(C-S-C) has shifted to lower side by 18-28 cm<sup>-1</sup> in the complexes on coordination of metal ions with sulphur of thiophene. The appearance of broad band around 3313,

3328 and 3350 cm<sup>-1</sup> in the spectra of complexes have been assigned to associated water molecule. In all complexes new bands at 490  $\pm$ 8 cm<sup>-1</sup> and 404 $\pm$ 2 cm<sup>-1</sup> are due to the formation of v(M-N) and v(M-S) bands respectively.

The IR spectrum of TCF Schiff base shows a strong band at 1626 cm<sup>-1</sup> due to v(C=N) azomethine group. On the chelation with metal ion, it has shifted down (11-38 cm<sup>-1</sup>) due to coordination of the azomethine nitrogen to the central metal ion. Thiophene ring v(C-S-C) shows absorption band at 842 cm<sup>-1</sup> in the Schiff base spectrum. This band shows lower shift by 24-27 cm<sup>-1</sup> in all complexes suggesting participation of thiophene v(C-S-C) sulphur in coordination. The appearance of broad band at 3397, 3387 and 3368 cm<sup>-1</sup> in complexes have been assigned to v(OH) water molecules **[17-20]**.

Compound	υ(C=N)	v(C-S-C)	$\upsilon(\mathrm{H_2O})$	υ(M-N)	υ(M-S)
[TCC]	1630	848	-	-	-
[Co(TCC)2]Cl2.3H2O	1603	820	3350	486	402
[Ni(TCC) <sub>2</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O	1608	830	3313	490	408
[Cu(TCC) <sub>2</sub> Cl <sub>2</sub> ]	1610	825	-	488	410
[TCF]	1626	842	-	-	-
[Co(TCF) <sub>2</sub> ]Cl <sub>2</sub> .2H <sub>2</sub> O	1600	816	3397	488	410
$[Ni(TCF)_2Cl_2].2H_2O$	1598	818	3387	485	408
[Cu(TCF)2Cl2].2H2O	1605	815	3368	482	406

Table 2. IR bands of Schiff base ligands and their complexes.

The IR data of both the Schiff base and its metal complexes show that the Schiff bases (TCC and TCF) is coordinated to the metal ion in bidentate manner with SN donor sites of thiophene sulphur and azomethine nitrogen.



Fig. 3. IR spectrum of TCC Schiff base ligand.

#### Electronic spectra and magnetic moment

The electronic spectral data of the metal complexes in DMSO solution are given in Table 3. The nature of the ligand field around the metal ion has been deduced from the electronic spectra. Magnetic moments of the compounds have also been calculated **[21]**. The equation for effective magnetic moment is given by;

$$\mu_{eff} = 2.839 (X_m \times T)^{1/2} BM$$

where T is the absolute temperature,  $\chi_m$  is the molar susceptibility.

The effective magnetic moment of transition elements is the sum of the spin and orbital moments, *i.e.*;

$$\mu_{\text{eff}} = (\mu_{s} + \mu_{L}) = [4S(S+1) + L(L+1)]^{1/2}$$

The electronic spectrum of Co(II) complex of TCC shows two bands of appreciable intensity at 15503 cm<sup>-1</sup> and 20125 cm<sup>-1</sup> which have tentatively been assigned to  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(F)$  (v<sub>2</sub>) and  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$  (v<sub>3</sub>) transitions. The magnetic moment is 4.35 B.M. Thus the tetrahedral geometry has been suggested for this complex. The electronic spectrum of Ni(II) complex of TCC, showed three bands at 11070 cm<sup>-1</sup>, 18816 cm<sup>-1</sup> and 24125 cm<sup>-1</sup> corresponding to transition  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$  (v<sub>1</sub>),  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$  (v<sub>2</sub>),  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(P)$  (v<sub>3</sub>) respectively. The magnetic moment is 3.19 B.M. These findings are in favor of an octahedral geometry for the Ni(II) complex. For Cu(II) complex of TCC, a single broad band at 13320 cm<sup>-1</sup> has been observed, this attributes to  $^2E_g {\rightarrow} ^2T_{2g}$  transition. Its magnetic moment is 1.85 B.M. Thus the octahedral geometry has been suggested for complex. The electronic spectrum of Co(II) complex of TCF shows two bands of appreciable intensity at 12360 cm<sup>-1</sup> and 19806 cm<sup>-1</sup> which have tentatively been assigned to  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(F)$  (v<sub>2</sub>) and  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$  (v<sub>3</sub>) transitions. The magnetic moment is 4.67 B.M. Thus, the tetrahedral geometry has been suggested for this complex. The electronic spectrum of Ni(II) complex of TCF exhibits three bands at 11220 cm<sup>-1</sup> and 20212 cm<sup>-1</sup> and 23645 cm<sup>-1</sup> which are assignable to  ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{2}g(F)$  $(v_1)$ ,  ${}^{3}A_2g(F) \rightarrow {}^{3}T_1g(F)$   $(v_2)$  and  ${}^{3}A_2g(F) \rightarrow {}^{3}T_1g(P)$   $(v_3)$ transition respectively. The magnetic moment is 3.14 B.M. These findings are in favour of an octahedral geometry for the Ni(II) complex. In the Cu(II) complex of TCF a single broad band at 16750 cm<sup>-1</sup> has been observed, this attributes to  ${}^{2}Eg \rightarrow {}^{2}T_{2g}$  transition. Its magnetic moment is 1.94 B.M. Thus the octahedral geometry has been suggested for complex [22-26].



Fig. 4. ESR spectrum of [Cu(TCC)<sub>2</sub>Cl<sub>2</sub>] complex

## ESR spectra

The ESR spectra of Cu(II) provide information about the extent of the delocalization of unpaired electron. The X-band ESR spectra of Cu(II) complexes were recorded in the

solid state at room temperature, their  $g_{\parallel}, g_{\perp}, \Delta g, g_{av}, G$  have been calculated. The values of ESR parameters  $g_{\parallel}, g_{\perp}, g_{av}, \Delta g, G$  for Cu(II) complex of TCC (**Fig. 4**) are 2.1775, 2.0977, 2.1030, 0.0526 and 1.83 respectively. Similarly, the corresponding values for Cu(II) complex of TCF (**Fig. 5**) are 2.2454, 2.0665, 2.1048, 0.7254 and 3.77 respectively.

ESR spectra of the complexes revealed two g values (g and  $g_{\perp}$ ). Since the  $g_{\parallel}$  and  $g_{\perp}$  values are closer to 2 and  $g_{\parallel}>g_{\perp}$  suggesting a tetragonal distortion around the Cu(II) ion. The trend  $g_{\parallel} > g_{\perp} > g_e(2.0023)$  shows that the unpaired electron is localized in  $d_X^2 - Y^2$  orbital in the ground state of Cu(II), spectra are characteristic of axial symmetry. The  $g_{\parallel}>2.3$  is characteristic of an ionic environment and  $g_{\parallel}<2.3$ indicates a covalent environment in metal ligand bonding. The  $g_{\parallel}$  values for these complexes are less than 2.3 suggesting the environment is covalent. The exchange coupling interaction between two Cu(II) ions is explained by Hathaway expression  $G = (g_{\parallel}-2.0023)/(g_{\perp}-2.0023).$ According to Hathaway, if the value G is greater than four (G>4.0), the exchange interaction is negligible; whereas when the value of G is less than four (G<4) a considerable exchange coupling is present in solid complex. The G values for these Cu(II) complexes are less than four indicate, considerable exchange interaction in the complexes [27-29].



Fig. 5. ESR spectrum of [Cu(TCF)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O complex

#### Thermal analyses

The thermal behavior of metal complexes shows that the hydrated complexes lose molecules of hydration first; followed by decomposition of ligand molecules in the subsequent steps.

The thermal degradation behavior of the Co(II) complex of TCC (**Fig. 6**) has been studied by thermogravimetric analysis. The thermogram of the complex shows a weight loss between 80-130 °C. This corresponds to loss of two lattice water molecules in the complex (Remaining Wt.%, Obs./Calcd., 92.5/91.86). After 260 °C, a gradual weight loss has been observed in general upto 490 °C, corresponding to the loss of partially decomposed ligand part from the complex (Remaining Wt.%, Obs./Calcd., 46.5/42.45). After this temperature a weight loss has been observed up to 600 °C, suggesting the elimination of the remaining part of the ligand. Above 600 °C, a constant weight region has been observed due to metal oxide, as a final pyrolysis product (Remaining Wt.%, Obs./Calcd., 24.3/20.63).

The thermogram of the Ni(II) complex of TCF shows (Fig. 7) that the complex loss in the weight during the temperature range 80-120 °C, approximately equal to two water molecules, assignable to lattice water in the complex (Remaining Wt.%, Obs./Calcd., 94.2/93.75). On increase in temperature above 240 °C, a speedy weight loss has been observed upto 430 °C, corresponding to the loss of partially decomposed ligand part from the complex (Remaining Wt.%, Obs./Calcd., 48.40/46.43). Above this temperature loss in weight has been occurs up to 610°C. This indicates the elimination of the remaining thermally degradable part of the complex. After 610 °C a horizontal curve has been observed which corresponds to a mixture of metal oxide as an ultimate pyrolysis product (Remaining Wt.%, Obs./Calcd., 22.3/19.82) [30-33].



Fig. 6. TG curve of [Co(TCC)<sub>2</sub>]Cl<sub>2</sub>.3H<sub>2</sub>O complex.



Fig. 7. TG curve of  $[Ni(TCF)_2Cl_2].2H_2O$  complex.

## X-ray diffraction study

X-ray diffraction was performed of metal complexes. The XRD patterns indicate crystalline nature for the complexes. X-ray powder diffractogram of the complexes were recorded using CuK $\alpha$  as source in the range 5°-90° (2 $\theta$ ). X-ray crystal system has been worked out by trial, error methods for finding the best fit between observed, calculated sin<sup>2</sup> $\theta$ . The diffractogram of Ni(II) complex of TCC shows 18 reflections. The observed values fit well in

the Tetragonal system and gives a unit cell with lattice constant a = b = 17.47 Å, c=12.23Å and cell volume V= 3732.60 Å<sup>3</sup>, Z= 6 (number of molecule per unit cell). The cell volume gives the observed value of density 1.688 g/cm<sup>3</sup>, while the calculated value of density has been found to be 1.684 gm/cm<sup>3</sup>. The observed and calculated values of density and sin<sup>2</sup> $\theta$  show good agreement.

The diffractogram of Co(II) complex of TCF (**Fig. 8**) has recorded 16 reflections. A comparison of the value reveals that there is a good agreement between calculated and observed value of  $\sin^2\theta$ . The observed values fit well in the Cubic system and gives a unit cell with lattice constant a = b = c = 27.14 Å, and cell volume V= 19990.77 Å<sup>3</sup>, Z= 28 (number of molecule per unit cell). The cell volume gives the observed value of density 1.675 g/cm<sup>3</sup>, while the calculated value of density has been found to be 1.675 gm/cm<sup>3</sup> [**34**, **35**].



Fig. 8. X-Ray Powder Diffractogram of [Co(TCF)2]Cl2.2H2O complex

#### Electrical conductivity

The temperature dependence of the solid state conductivity ( $\sigma$ ) of the compounds in their compressed pellet form have been measured at fixed frequency 1KHz in the temperature range 297-413 K. the values of the solid state electrical conductivity of the Schiff base, its complexes increases with increasing temperature, decreases upon cooling over the studies temperature range indicating their semiconducting behavior.

#### $\sigma = \sigma_0 \exp(-Ea/KT)$

where Ea is the thermal activation energy of conduction,  $\sigma_o$  is the conductivity constant, K is the Boltzman constant. The lots of  $\sigma$  vs 1000/T for all the compounds are found to be linear over a studies temperature range. The room temperature electrical conductivity of all the compounds lies in the range  $2.321 \times 10^{-6}$ - $6.142 \times 10^{-10}$  ohm<sup>-1</sup>cm<sup>-1</sup>. These values show their semi-conducting nature. The electrical conductivity at room temperature for the complexes of TCC are Co>Cu>Ni and for the metal complexes of TCF are Co>Ni>Cu. The activation energy of the compound lies in the range 0.241-0.775 eV [**36-38**]. The confirming of the temperature dependence conductivity of the compounds

was also checked by the repeating of the conductivity measurements.

## Conclusion

In the present research studies, our efforts are synthesized of some newly compounds from the conventional as well as microwave methods. These synthesized compounds Characterized by various physicochemical and spectral analyses. The synthesized Schiff base ligands bind with the metal ions in a bidentate manner, with SN donor sites of thiophene-S and azomethine-N. FAB-mass and thermal data show degradation pattern of the complexes. Thermogravimetric studied of the complexes also helped to characterize of the complexes. The XRD patterns indicate crystalline nature of the complexes. Electrical conductivity data suggest that all the complexes fall in the semiconducting range.

#### Acknowledgements

We are thankful to I.I.T. Mumbai for ESR analysis. We also acknowledge SAIF, CDRI Lucknow for micro analysis and spectral analyses. Thanks are also due to the Head, Department of Chemistry, Botany and Physics, Dr. Hari Singh Gour University, Sagar (M.P.) for providing Laboratory facilities.

## Reference

- Chandra, S.; Kumar, U. Spectrochim. Acta. 2005, 61A, 219. DOI: <u>10.1016/j.saa.2004.03.036</u>
- Shirodkar, S.G.; Mane, P.S.; Chondhekar, T.K. Indian J. Chem. 2001, 40, 1114
- 3. Soliman, A.A.; Mohamed, G.G. *Thermochim Acta* **2004**, 421, 151. **DOI:**10.1016/j.tca.2004.03.010
- Mishra, A.P.; Jain, R. J. Saudi Chem. Soc. (In press). DOI:10.1016/j.jscs.2011.09.013
- Coombs, R.R.; Westcott, S.A.; Decken, A.; Baerlocher, F.J. *Trans. Met. Chem.* 2005, 30, 411.
- **DOI:** <u>10.1007/s11243-004-7625-4</u>
  Spinu, C.; Kriza, A.; Spinu, L. *Acta Chim. Slov.* **2001**, 48, 257.
- Raman, N.; Raja, S. J.; Joseph, J.; Raja, J.D. J. Chil. Chem. Soc. 2007, 52, 1138.
- Omar, M.M.; Mohammed, G.G.; Spectrochim. Acta 2005, 61A, 929. DOI: <u>10.1016/j.saa.2004.05.040</u>
- 9. Mahajan, K.; Fahmi, N.; Singh, R.V. Indian J. Chem. 2007, 46A, 1221.
- Sharma, A.K.; Mishra, A.K. Adv. Mat. Lett. 2010, 1(1), 59. DOI: <u>10.5185/amlett.2010.4120</u>
- Sharma, K.; Singh, R.; Fahmi, N.; Singh, R.V. Spectrochim. Acta. 2010, 75A, 422.
   DOI: <u>10.1016/j.saa.2009.10.052</u>
- 12. Garg, R.; Saini, M.K.; Fahmi, N.; Singh, R.V. Trans. Met. Chem. 2006, 31, 362.
- DOI: <u>10.1007/s11243-005-0001-1</u>
  13. Mahajan, K.; Swami, M.; Singh, R.V. *Russ. J. Coord. Chem.* **2009**, 35, 179.
- **DOI:** <u>10.1134/S1070328409030038</u> 14. Mishra, A.P.; Tiwari, A.; Gupta, S.; Jain, R. *E-J. Chem.* Accepted,
- **2012**. 15. Dubey, R.K.; Dubey, U.K.; Mishra, C.M. *Indian J. Chem.*, **2008**,
- 47A, 1208.
  16. Mishra, A.P.; Soni, M. *Metal Based Drug*. 2008. DOI:<u>10.1155/2008/875410</u>
- Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5<sup>th</sup> ed. John Wiley and Sons, Part A & B, New York, **1998**.
- Abdallah, S.M.; Zyed, M.A.; Mohammed, G.G. Arabian J. Chem. 2010, 3, 103.
   DOI: <u>10.1016/j.arabjc.2010.02.006</u>

- Neelakantan, M.A.; Marriappan, S.S.; Dharmaraja, J.; Jeyakumar, T.; Muthukumaran, K. *Spectrochim. Acta. A* 2008, 71, 628.
   DOI: <u>10.1016/j.saa.2008.01.023</u>
- Garg, B.S.; Kumar, D.N. Spectrochim. Acta 2003, 59A, 229. DOI:10.1016/S1386-1425(02)00142-7
- Dutta, R.L.; Syamal, A. *Elements of Magneto Chemistry*, 2<sup>nd</sup> ed. Affiliated East West Press, New Delhi, **1993**.
- A.B.P. Lever, Inorganic Electronic Spectroscopy, 2<sup>nd</sup> ed. Elsevier, New York, 1984.
- 23. Chandra, S.; Sharma, A.K. J. Coord. Chem. **2009**, 62, 3688 DOI: <u>10.1080/00958970903121305</u>
- Mishra, A.P.; Mishra, R.K.; Shrivastava, S.P. J. Serb. Chem. Soc. 2009, 74, 523. DOI: 10.2298/JSC0905523M
- Ourari, A.; Ouari, K.; Moumeni, W.; Sibous, L.; Bouet, G.M.; Khan, M.A. *Trans. Met. Chem.* **2006**, 31, 169.
   **DOI:** 10.1007/s11243-005-6334-y
- Chandra, S.; Jain, D.; Sharma, A.K.; Sharma, P. Molecules 2009, 14, 174.

DOI: 10.3390/molecules14010174

- Hathaway, B.J. Comprehensive Coordination Chemistry, Vol. 5, Pergamon Press (U.K.), 1987, 534.
- 28. Mishra, A.P.; Pandey, L.R. Indian J. Chem. 2005, 44A, 94.
- 29. Hathaway, B.J.; Billing, D.E. Coordination Chemistry Review 1970, 5, 143.
- Mohamed, G.G.; Omar, M.M.; Hindy, A.M. Turk J. Chem. 2006, 30, 361.
- Mohamed, G.G.; Omar, M.M.; Ibrahim, A.A. *Eur. J. Med. Chem.* 2009, 44, 4801.
   DOI: <u>10.1016/j.ejmech.2009.07.028</u>
- Wang, Y.F.; Liu, J.F.; Xian, H.D.; Zhao, G.L. Molecules 2009, 14, 2582.
- **DOI:** <u>10.3390/molecules14072582</u> 33. Al-Shihri, A. S. M.; Abdel-Fattah, H. M. J. Therm. Anal. Cal. **2003**,
- Al-Shihri, A. S. M.; Abdel-Fattan, H. M. J. Therm. Anal. Cal. 2003, 71, 243.
   DOI: 10.1023/A:1022880615841
- 34. M.S. Sujamol; C.J. Athira; Y. Sindhu; K. Mohanan; Spectrochim. Acta 2010, 75A, 106.
   DOI: 10.1016/j.saa.2009.09.050
- 35. Patange, V.N.; Arbad, B.R., J. Indian Chem. Soc., 2007, 84, 1096.
- 36. Mishra A.P. and Pandey L.R., Indian J. Chem., 2005, 44A, 1800.
- 37. Kumar, P.; Singh, B.P.; Sinha, T.P., Singh, N.K. Adv. Mat. Lett. 2011, 2(1), 76.
- DOI:<u>10.5185/amlett.2010.11176</u>
   38. Makode, J.T.; Yaul, A.R.; Bhadange, S.G.; Aswar, A.S. *Russ. J. Inorg. Chem.*, **2009**, 54, 1372.
   DOI: 10.1134/S003602360909006X

## Advanced Materials Letters

#### Publish your article in this journal

ADVANCED MATERIALS Letters is an international journal published quarterly. The journal is intended to provide top-quality peer-reviewed research papers in the fascinating field of materials science particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications of materials. All articles are indexed on various databases including DOAJ and are available for download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review articles, research articles, notes, letter to editor and short communications.

