

## Research Article

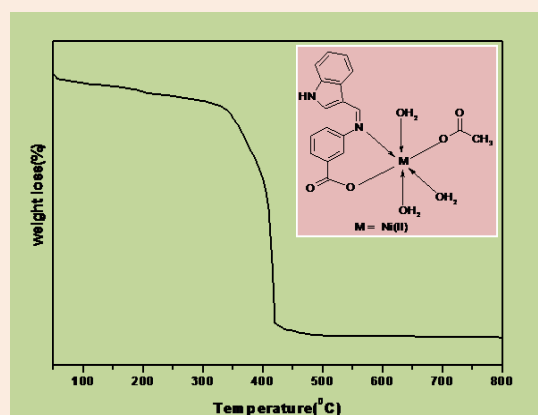
## Evaluation on Structural and Thermoanalytical Properties of a Novel Heterocyclic Schiff Base Derived from 3-Formylindole and its Metal Chelates

Aby Paul, Joby Thomas K\*, Sini Varghese C, Reeja Johnson

Research Division, Department of Chemistry, St. Thomas' College (Autonomous), Thrissur, Kerala

**Abstract**

A novel Schiff base derived from 3-formylindole and 3-aminobenzoic acid and its Mn(II), Ni(II) and Cu(II) transition metal complexes were synthesized. Structures of the ligand and complexes were derived on the basis of various analytical techniques such as  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, infrared, mass, electronic spectroscopy, elemental, magnetic and conductance studies. Structural evaluation established that a 1:1 stoichiometry exists between the metal and ligand and the chelates possess general formula  $[\text{ML}(\text{Ac})(\text{H}_2\text{O})_3]$ . Geometry of all the complexes was found to be octahedral. Thermal decomposition kinetics and mechanism of the metal chelates were studied by TG and DTA techniques. The TG curve of all chelates showed a two stage decomposition pattern in the TG trace which is supported by DTA data. The decomposition of these chelates was found to follow first order kinetics, but the first stage decomposition of Mn(II) was  $2/3$  order of reaction.



**Keywords:** 3-formylindole, 3-amino benzoic acid, metal complexes, TG studies

**\*Correspondence**

Joby Thomas K,  
Email: drjobythomask@gmail.com

**Introduction**

Schiff bases, are organic molecules possessing azomethine linkage (C=N), have innumerable applications [1]. Metal complexes of Schiff bases play vital role in the development of coordination chemistry. In recent days scientists are more interested in heterocyclic Schiff bases [2-4] and their metal complexes [5,6]. The Schiff base complexes derived from 3-aminobenzoic acid are of great importance since they have potential applications in biological systems and chemical fields [7,8]. In the present course of investigation, a novel potential Schiff base 3-formylindole-3-aminobenzoic acid (3FI3ABA) and its metal complexes of Mn(II), Ni(II) and Cu(II) were synthesized and characterized using various analytical tools and physicochemical methods. Thermal decomposition kinetics and mechanism of the metal chelates were also studied by TG and DTA techniques.

**Experimental**

An ethanolic solution of 3-aminobenzoic acid (2mM) was mixed with a solution of 3-formylindole (2mM) in ethanol and refluxed for four hours on a water bath. The resulting solution was concentrated and cooled in an ice bath. The precipitate formed was filtered washed with ethanol and dried. Mn(II), Ni(II) and Cu(II) complexes of 3-formylindole-3-aminobenzoic acid (3FI3ABA) were prepared by mixing ethanolic solutions of metal acetate (2mM), 3-amino benzoic acid (2mM) and 3-formylindole (2mM). The resulting solution was refluxed for about 3 hours, concentrated and cooled in an ice bath. The complex formed was filtered, washed with ethanol and ether and dried. Thermogravimetric studies of the metal chelates were performed in air atmosphere with the help of Perkin Elmer 7 series Thermal analyzer system in conjunction with 951TG analyzer at a heating rate of  $10^{\circ}\text{C}$

## Results and Discussion

The IR spectrum of the Schiff base showed the characteristic C=N stretching vibration in the region of  $1600\text{cm}^{-1}$ . The -OH group of the carboxylic acid part appeared in the region  $3000\text{cm}^{-1}$ . In the electronic spectrum, the absorption bands because of the  $n\rightarrow\sigma^*$ ,  $\pi\rightarrow\pi^*$  and  $n\rightarrow\pi^*$  transitions, were observed at 38500, 31300 and  $28900\text{cm}^{-1}$  respectively. The  $^1\text{H}$  NMR (DMSO- $d_6$ ) signal for proton of the carboxylic acid appeared as a singlet at  $\delta$  11.99. The aromatic protons of both indole and benzene rings resonated in the region  $\delta$  7.14-8.19. The  $^{13}\text{C}$  NMR spectrum of the Schiff base, 3FI3ABA, showed the carboxylic acid carbon signal at 187.56ppm. A peak at 130.32ppm can be assigned to the azomethine carbon. As expected, the  $^{13}\text{C}$  NMR spectrum exhibited sixteen characteristic signals which confirmed the presence of sixteen type carbon atoms of different chemical environment. In the high resolution mass spectrum of the ligand, the peak due to molecular ion was found to appear at  $m/z$  264, which acted as the base peak. The M+1 peak was observed at  $m/z$  265 with a relative abundance of 15.8 which confirms the presence of sixteen carbon atoms in the Schiff base. On the basis of the above results, the structure of the ligand 3FI3ABA was confirmed and shown in the Fig.1.

All complexes are coloured, non hygroscopic solids and photo-stable. They are insoluble in methanol, ethanol, petroleum ether, diethyl ether etc, but appreciably soluble in DMSO, DMF etc. The elemental analysis, molar conductance and magnetic moment data of the complexes are presented in Table 1.

**Table 1** Microanalytical, magnetic and conductance data of transition metal complexes of 3-formylindole-3-aminobenzoic acid (3FI3ABA)

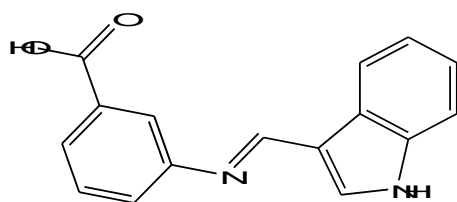
Complex	Colour & M.P ( $^{\circ}\text{C}$ )	Metal %	C %	H %	N %	$\mu_{\text{eff}}$ (BM)	Molar conductance ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )
3FI3ABA (LH)	Brown 200	-	72.16 (72.72)	4.30 (4.54)	10.35 (10.60)	-	-
[MnLAc(H <sub>2</sub> O) <sub>3</sub> ]	Brown 330	12.51 (12.76)	50.57 (50.10)	4.68 (4.64)	6.20 (6.49)	5.59	12
[CuLAc(H <sub>2</sub> O) <sub>3</sub> ]	Green 360	14.20 (14.44)	49.39 (49.09)	4.71 (4.54)	6.85 (6.36)	1.82	14
[NiLAc(H <sub>2</sub> O) <sub>3</sub> ]	Green 290	13.45 (13.56)	49.31 (49.65)	4.50 (4.59)	6.79 (6.43)	3.68	5

The very low values of molar conductance indicate that these complexes are non electrolytes in DMSO. The effective magnetic moment ( $\mu_{\text{eff}}$ ) of Mn(II) complex indicate  $^6\text{A}_{1g}$  as ground state for  $d^5$  configuration in high spin octahedral stereochemistry[9]. The Ni(II) complex exhibited the magnetic moment value of 3.68BM and octahedral geometry is suggested. The value for  $\mu_{\text{eff}}$  for Cu(II) complex obtained was slightly higher than the spin only magnetic moment (1.8BM) expected for  $d^9$  configuration with one unpaired electron[10,11]. This accounts the slight orbital contribution to the spin only value and the absence of spin-spin interactions. Therefore octahedral geometry is suggested for this complex. Mn(II) complex of 3FI3ABA exhibited three bands at 12600, 13200,  $20100\text{cm}^{-1}$  in its electronic spectrum. These bands can be assigned to  $^6\text{A}_{1g}\rightarrow^4\text{T}_{1g}(\text{G})$ ,  $^6\text{A}_{1g}\rightarrow^4\text{T}_{2g}(\text{G})$  and  $^6\text{A}_{1g}\rightarrow^4\text{E}_g(\text{G})$  transitions respectively, which is in accordance with Mn(II) high spin octahedral geometry. A signal at  $22300\text{cm}^{-1}$  is shown by the copper complex in its electronic spectrum is attributed to the charge transfer band. The electronic spectral data obtained were found to agree with conclusions arrived from magnetic susceptibility measurements.

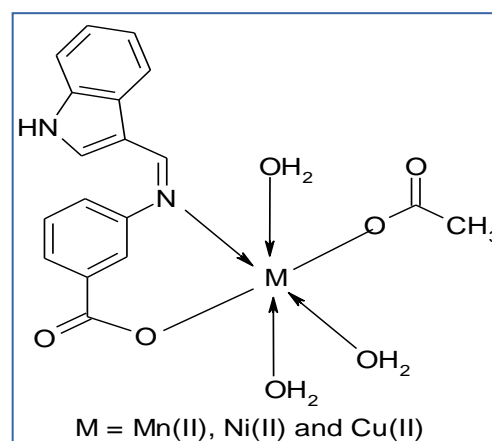
Characteristic infrared bands of the ligand and complexes are given in Table 2. A shift of carboxylate stretching bands to the lower frequencies in the IR spectra of complexes indicates the chelation of the ligand to metal ion through the carboxylate oxygen.  $\nu_{C=N}$  of the Schiff base also underwent shift to lower frequencies which shows the coordination of nitrogen atom of the azomethine linkage to the metal atom, during complexation[12]. The frequencies of symmetric and asymmetric stretching vibrations of the carboxylate group exhibit a difference of about  $200\text{cm}^{-1}$  which suggest the monodentate nature of carboxylate part[13]. The presence of coordinated water molecules in the complexes was confirmed by a broad band around  $3300\text{-}3400\text{cm}^{-1}$ . From the spectroscopic and magnetic studies octahedral geometries can be assigned to the Mn(II), Ni(II) and Cu(II) complexes of 3FI3ABA (Fig. 2)

**Table 2** Characteristic infrared absorption frequencies of 3FI3ABA and its transition metal complexes

Complex	$\nu_{\text{H}_2\text{O}}$	$\nu_{\text{COO}}$ (asym)	$\nu_{\text{C=N}}$	$\nu_{\text{COO}}$ (sym)	$\nu_{\text{C-O}}$	In plane bending	Out of plane bending	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
3FI3ABA (LH)	-	1668	1600	1498	1222	1157	941, 754	-	-
[MnLAc(H <sub>2</sub> O) <sub>3</sub> ]	3354	1573	1544	1452	1242	1124	900, 777	680	525
[NiLAc(H <sub>2</sub> O) <sub>3</sub> ]	3396	1633	1541	1450	1247	1028	779	678	522
[CuLAc(H <sub>2</sub> O) <sub>3</sub> ]	3412	1629	1573	1454	1240	1149	796, 759	678	541



**Figure 1** Structure of 3FI3ABA

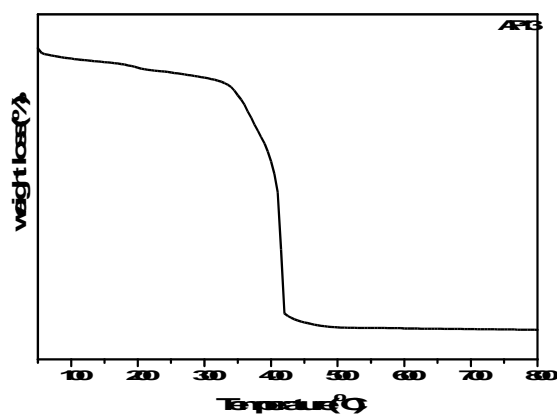


**Figure 2** Structure of Mn(II), Ni(II) and Cu(II) complexes

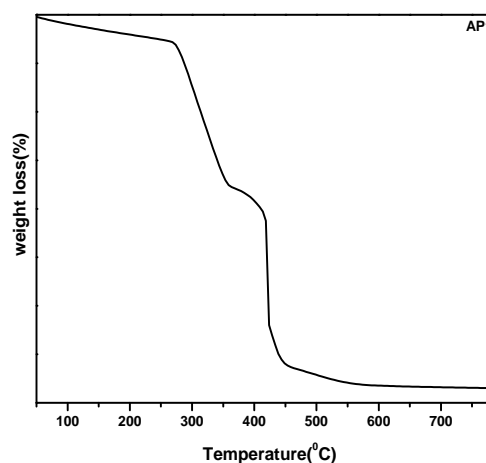
### Thermal decomposition studies

Mn(II) complex of 3FI3ABA gives a two clear cut and non overlapping stages of decomposition (Fig.3). The three water molecules are lost in the first stage with the completion temperature  $330^{\circ}\text{C}$ . In the second stage, the ligand as well as the acetate group is removed with a procedural temperature range of  $330\text{-}435^{\circ}\text{C}$ . The Ni(II) complex, having the formula  $[\text{NiLAc}(\text{H}_2\text{O})_3]$  exhibits a two stage pattern of decomposition. Both stages have two sub stages (Fig.4). In the first stage decomposition, there is a loss of three coordinated water molecules and indole moiety of the ligand from the complex. The second stage shows the removal of aminobenzoic acid part of the ligand and the acetate

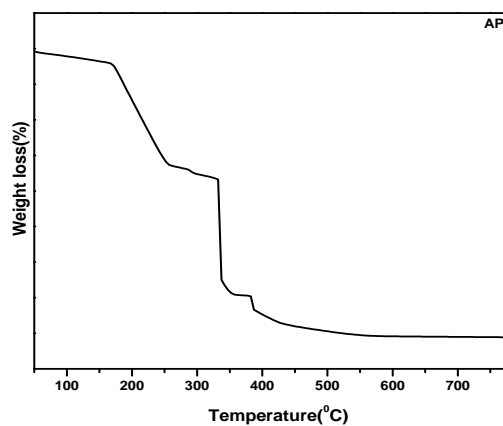
moieties. The final mass loss agrees with the values calculated for the conversion of the complex to its oxide (NiO). Similar pattern of decomposition is also exhibited by the copper complex of the ligand 3FI3ABA (Fig.5). The mass loss at the end of second stage as read from the TG curve is 78.25%, while the theoretical loss in mass for the conversion of  $[\text{CuLAc}(\text{H}_2\text{O})_3]$  to CuO is 78.40%.



**Figure 3** TG curve of  $[\text{MnLAc}(\text{H}_2\text{O})_3]$  of the Schiff base, 3FI3ABA



**Figure 4** TG curve of  $[\text{NiLAc}(\text{H}_2\text{O})_3]$  of the Schiff base, 3FI3ABA



**Figure 5** TG curve of  $[\text{CuLAc}(\text{H}_2\text{O})_3]$  of the Schiff base, 3FI3ABA

Based on the experimental results, the relative thermal stability[14,15] of these chelates can be given as  $[\text{CuLAc}(\text{H}_2\text{O})_3] < [\text{NiLAc}(\text{H}_2\text{O})_3] < [\text{MnLAc}(\text{H}_2\text{O})_3]$ . Thermal decomposition data of the two metal chelates are represented in Table 3. The non-isothermal TG curves have been subjected to mathematical analysis using the integral method of Coats-Redfern[16-20] and the activation parameters have been evaluated for all these complexes. The most suitable parameters were selected with the aid of correlation coefficient. The mechanism of decomposition has been established from the TG data using the nine mechanistic equations in comparison with the integral method [21-24] (Coats and Redfern). The kinetic data obtained by nine mechanistic equations for Mn(II), Ni(II) and Cu(II) complexes is displayed in the Table 4. Correlation studies revealed that all decomposition stages of these chelates obey the relation  $-\ln(1-\alpha) = kt$ , i.e. Mampel equation (Random nucleation; one nucleus at each particle), where  $\alpha$  is the fractional decomposition, at time  $t$ , while the first stage decomposition of Mn(II) complex obey phase boundary reaction.

**Table 3** Thermal decomposition data of Mn(II), Ni(II) and Cu(II) complexes of 3-formylindole-3-amino benzoic acid

Complex	Stage	Temp range in TG (°C)	Peak temp in TG (°C)	Peak temp in DTA (°C)	Loss of mass %		Probable assignment
					From TG & (Cald.)	From Pyrolysis	
[MnLAc(H <sub>2</sub> O) <sub>3</sub> ]	I	50-330	200	210	11.88 (12.53)	-	Loss of 3H <sub>2</sub> O
	II	330-435	405	412	75.33 (74.71)	-	Loss of L and acetate
					87.21 (87.24)	87.49	
[NiLAc(H <sub>2</sub> O) <sub>3</sub> ]	Ia	48-278	190	198	7.29 (7.36)	-	
	Ib	278-398	317	328	30.89 (30.81)	-	Loss of 3H <sub>2</sub> O+ indole moiety of L
	IIa	398-448	423	431	33.65 (34.02)	-	
	IIb	448-998	492	497	6.94 (6.21)	-	Loss of aminobenzoic acid part of L + acetate
				78.77 (78.40)	79.22		
[CuLAc(H <sub>2</sub> O) <sub>3</sub> ]	Ia	47-167	145	150	4.13 (4.09)	-	
	Ib	167-282	210	218	29.70 (30.45)	-	Loss of 2H <sub>2</sub> O + indole moiety of L
	IIa	282-352	332	337	34.87 (34.09)	-	
	IIb	352-457	387	392	9.55 (9.77)	-	Loss of aminobenzoic acid part of L+ H <sub>2</sub> O+ acetate
				78.25 (78.40)	78.29		

**Table 4** Kinetic parameters of the decomposition of Mn(II), Ni(II) and Cu(II) complexes of 3-formylindole-3-aminobenzoic acid from TG using non mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

Complex (stage)	Non-mechanistic/ mechanistic equation	Kinetic parameters*				Order (n)
		E	A	$\Delta S$	R	
[MnLac(H <sub>2</sub> O) <sub>3</sub> ] Stage I	Coats-Redfern	5.11	1.2x10 <sup>-3</sup>	-304.656	0.9860	2/3
	Equation IX	5.11	4.01x10 <sup>-4</sup>	-313.78	0.9860	
Stage II	Coats-Redfern	84.68	2.04x10 <sup>4</sup>	-169.209	0.9823	1
	Equation V	84.68	2.04x10 <sup>4</sup>	-169.209	0.9823	
[NiLac(H <sub>2</sub> O) <sub>3</sub> ] Stage Ib	Coats-Redfern	93.56	4.59x10 <sup>5</sup>	-142.19	0.9676	1
	Equation V	93.56	4.59x10 <sup>5</sup>	-142.19	0.9676	
Stage IIa	Coats-Redfern	617.13	1.82x10 <sup>44</sup>	595.34	0.9350	1
	Equation V	617.13	1.82x10 <sup>44</sup>	595.34	0.9350	
[CuLac(H <sub>2</sub> O) <sub>3</sub> ] Stage Ib	Coats-Redfern	77.11	7.09x10 <sup>5</sup>	-136.9	0.9943	1
	Equation V	77.11	7.09x10 <sup>5</sup>	-136.9	0.9943	
Stage IIa	Coats-Redfern	124.3	1.13x10 <sup>9</sup>	-77.42	0.9999	1
	Equation V	124.3	1.13x10 <sup>9</sup>	-77.42	0.9999	

\*E in kJmol<sup>-1</sup>; A in s<sup>-1</sup>,  $\Delta S$  in JK<sup>-1</sup>mol

## References

- [1] M. Jayandran, M. Haneefa *Chem Sci Rev Lett* 2014, 3(12), 1050.
- [2] V. P. Raphael, K. J. Thomas, K.S. Shaju, A. Paul, *Res. Chem. Intermed.*, 2013,39(2).
- [3] K.S. Shaju, K. J. Thomas, V. P Raphael, A. Paul, *Orient. J. Chem.*, 2014, 30-2, 807.
- [4] K. Nimmy, K. J. Thomas, V.P. Raphael, K.S. Shaju, *Indian. J. Mater. Sci.*, vol. 2014, Article ID 124065, 6 pages, doi:10.1155/2014/1240652014.
- [5] D. X. West, *Coord. Chem Rev.*, 1993, 123, 49.
- [6] S. Pandhye, G.B. Koffman, *Coord. Chem. Rev.*, 1985, 63, 127.
- [7] K. J. Thomas, G. Parameswaran, *Asian. J. Chem.*, 2002, 14, 1370.
- [8] K. S. Jacob, G. Parameswaran, *Corro. Sci.*, 2010, 52, 24.
- [9] K. S. Siddiqui, K. Sadaf, S. A. Nami, *J. Inclusion Phenom. Macrocyclic chem.*, 2005, 55, 359.
- [10] M.S.S. Babu, K.H. Reddy, P.G. Krishna, *Polyhedron*, 2007, 26, 572.
- [11] S. Srivastava, A. Kalam, *Synth. Tract. Inorg. Met. Org. Che.*, 2004, 24, 613.
- [12] J. M. Sece, M. Quiros, M. J. G. Gaemendia, *Polyhedron*, 2000, 19, 1005.
- [13] A. M. El-Roudi, *Faculty Science*, Assiut University, 1989, 18, 77.
- [14] R. Seshadri Naidu, R. Raghava Naidu, *Indian. J. Chem.*, 1977, 15A, 652.

- [15] R.S. Naidu, E.N. Rao, *Thermo chim. Acta.*, 1988,131, 299., 1989,140, 97.  
[16] A. W. Coats, J. P. Redfern, *Nature*, London, 1965, 68, 201.  
[17] R. C. Mactenzic, *Differential Thermal Analysis*, Academic Press, London, 1970, 1, 17.  
[18] C. Daval, *Inorganic Thermogravimetric Analysis*, Elsevier, New York, 2<sup>nd</sup> Ed., 1963.  
[19] K. N. Johri, B. S. Arora, *Thermochim. Acta*, 1982, 54, 237.  
[20] L. Pardeshi, R. A. Bhobe, *Acta Cienc. Indica.*, 1983, 9, 18.  
[21] J. Sestak, *Talanta*, 1966, 13, 567.  
[22] J. Sestak, *Silikaty*, 1967, 11, 153.  
[23] A. Nagajothi, A. Kiruthika, S. Chithra, K. Parameswari, *Res. J. Chem. Sci.*, 2013,3-2, 35.  
[24] S. Poonam, R. Y. Amit, N. B. Jayashree, S. A. Anand, *World. App. Sci. J.*, 2010, 9-11, 1301.

© 2015, by the Authors. The articles published from this journal are distributed to the public under “**Creative Commons Attribution License**” (<http://creativecommons.org/licenses/by/3.0/>). Therefore, upon proper citation of the original work, all the articles can be used without any restriction or can be distributed in any medium in any form.

#### Publication History

Received 05<sup>th</sup> Feb 2015  
Revised 16<sup>th</sup> Feb 2015  
Accepted 11<sup>th</sup> Mar 2015  
Online 30<sup>th</sup> Mar 2015