This article was downloaded by: [Nipissing University] On: 17 October 2014, At: 12:27 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt20</u>

## Synthesis, Spectroscopic, Thermal, and Photostability Studies of 2-aminobenzaldehyde Phenylhydrazone (2ABPH) as Fluorescent Dye and their Cu(II), Co(II), and Mn(II) Complexes

Moamen S. Refat <sup>a b</sup> , Hamada M.A. Killa <sup>c</sup> , Asmaa F. Mansour <sup>d</sup> & Hammad Fetooh <sup>c</sup> <sup>a</sup> Department of Chemistry, Faculty of Science , Port Said University , Port Said, Egypt <sup>b</sup> Department of Chemistry, Faculty of Science , Taif University , Taif, Kingdom Saudi Arabia

<sup>c</sup> Department of Chemistry, Faculty of Science, Zagazig University, Zagazig, Egypt <sup>d</sup> Department of Physics, Faculty of Science, Zagazig University, Zagazig, Egypt Published online: 12 Apr 2011.

To cite this article: Moamen S. Refat , Hamada M.A. Killa , Asmaa F. Mansour & Hammad Fetooh (2011) Synthesis, Spectroscopic, Thermal, and Photostability Studies of 2-aminobenzaldehyde Phenylhydrazone (2ABPH) as Fluorescent Dye and their Cu(II), Co(II), and Mn(II) Complexes, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 41:3, 295-308

To link to this article: <u>http://dx.doi.org/10.1080/15533174.2011.555863</u>

#### PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <a href="http://www.tandfonline.com/page/terms-and-conditions">http://www.tandfonline.com/page/terms-and-conditions</a>



### Synthesis, Spectroscopic, Thermal, and Photostability Studies of 2-aminobenzaldehyde Phenylhydrazone (2ABPH) as Fluorescent Dye and their Cu(II), Co(II), and Mn(II) Complexes

Moamen S. Refat,<sup>1,2</sup> Hamada M. A. Killa,<sup>3</sup> Asmaa F. Mansour,<sup>4</sup> and Hammad Fetooh<sup>3</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Port Said University, Port Said, Egypt

<sup>2</sup>Department of Chemistry, Faculty of Science, Taif University, Taif, Kingdom Saudi Arabia

<sup>3</sup>Department of Chemistry, Faculty of Science, Zagazig University, Zagazig, Egypt

<sup>4</sup>Department of Physics, Faculty of Science, Zagazig University, Zagazig, Egypt

Herein, the 2-aminobenzaldehyde phenylhydrazone (2ABPH) Schiff base and their mononuclear Mn(II), Co(II), and Cu(II) complexes were reported. The structures of the complexes have been elucidated by elemental analysis, molar conductivity, magnetic properties, infrared, electronic, mass spectra, and thermal studies. The stoichiometries of the 2ABPH complexes accordance of the mentioned analysis give the general formula  $[M(2ABPH)_2(Cl)_2].xH_2O$  (where M is Mn(II), Co(II), Cu(II), and x = 1, 4 and 6). The photo stabilities of the Schiff base and their complexes were examined.

Keywords 2-aminobenzaldehyde phenylhydrazone, photo stabilities, Schiff base, thermal studies

#### INTRODUCTION

2-aminobenzaldehyde phenylhydrazone,  $C_{13}H_{13}N_3$ ; (MW = 211.27), is called Nitrin. It was prepared by refluxing 2nitrobenzaldehyde with phenylhydrazine.<sup>[1]</sup> This compound is used in the detection of nitrites and colibacilli in urine.<sup>[2]</sup>

A large number of publications,<sup>[3–10]</sup> ranging from purely synthetic to modern physicochemical and biochemically relevant studies of metal complexes of Schiff bases, reveal that such complexes have occupied a central role in the development of coordination chemistry. These complexes have been studied toward the behavior,<sup>[11]</sup> their coordination,<sup>[12–14]</sup> stoichiometry,<sup>[15]</sup> and antibacterial activity.<sup>[16–18]</sup> Schiff bases have been widely discussed due to their selective chelation to certain metal ions depending on the number, kind, and position of their donor atoms.<sup>[19–21]</sup> Schiff base complexes of trivalent lanthanide ions have an important role in the development of photonic light converting device and sensors,<sup>[22,23]</sup> sensitizer for photodynamic therapy, and biomedical diagnostics,<sup>[24,25]</sup> among others, show that extensive work with Schiff base complexes has been done and is still in progress. In view of these findings and in continuation to the authors' previous work on the Schiff bases,<sup>[26–31]</sup> this piece of work has been devoted with the aim to synthesize some Mn(II), Co(II), and Cu(II) complexes with 2-aminobenzaldehyde phenylhydrazone (2ABPH) Schiff base ligand, and examine their physical properties (photo stability of the Schiff base before and after complexation) involving spectral behaviors.

#### MATERIALS AND METHODS

The general chemical structure of the synthesized of 2aminobenzaldehyde phenyl hydrazone (2ABPH) is given in (Figure 1).

## Synthesized 2-aminobenzaldehyde Phenylhydrazone (2ABPH)

To 100 ml of distilled water in a 250 ml beaker are added 1 g. of crystalline sodium sulfide nonahydrate and 0.5 gm of sulfur. The mixture is heated on a water bath for 15–20 minutes with occasional stirring, and then poured into a 500 ml roundbottomed flask containing a hot solution of (3.02 g, 0.02 mol) of *o*-Nitrobenzaldehyde and (2.20 ml, 0.02 mol) phenyl hydrazine in 100 ml of methanol. A reflux condenser is attached, and the mixture is heated under reflux for 3 hours. The solution is rapidly chilled in an ice bath with occasional vigorous shaking and stirring to induce crystallization. After 2 hours in the ice bath, the deep red crystals of 2-aminobenzaldehyde phenylhydrazone are collected on a Büchner funnel and washed with 50 ml of

Received 17 July 2010; accepted 31 October 2010.

Address correspondence to Moamen S. Refat, Department of Chemistry, Faculty of Science, Port Said University, Port Said, Egypt. E-mail: msrefat@yahoo.com

ice water to remove sodium sulfide. The product is immediately placed in a vacuum desiccator over solid calcium chloride pellets for 24 hours. Re-crystallization was carried out in methanol. The yield of 2-aminobenzaldehyde phenylhydrazone produced is 75% with m.p =  $130^{\circ}$ C. The procedures of the synthesized of (2ABPH) described as follows:



#### Cu(II), Co(II), and Mn(II) Complexes of (2ABPH)

Selected transition metal chloride salts like (CoCl<sub>2</sub>.6H<sub>2</sub>O, MnCl<sub>2</sub>.4H<sub>2</sub>O and CuCl<sub>2</sub>.H<sub>2</sub>O (Fluka)) and all the used solvents were of pure or spectroscopic grade.

These complexes were synthesized by dissolving the appropriate amount of 2ABPH ligand (1 mmole, in 25ml 99% methanol) with stirring and heating on a hot-plate at 60–70°C till completely soluble. Then added the metal ions as solid (0.5 mmole) and continued stirring with heating till all metallic-salts are dissolved. The volume of the obtained solutions was reduced to one-half by evaporation followed by adding 20 ml acetone with stirring and heating carefully till obtaining the colored solid complexes of 2ABPH. The Cu(II), Co(II), and



FIG. 1. Structure of synthesized 2-aminobenzaldehyde phenylhydrazone (2ABPH).

Mn(II) complexes isolated as powered materials. At the time of addition: with respect to Co(II)/2ABPH complex, the color of solution before precipitation was yellowish-orange and after precipitated, became greenish-brown ppt, the m.p =  $136^{\circ}$ C and % yield = 0.321g (89%), for Mn(II)/2ABPH complex, the color of complex before precipitation was orange-yellow and so orange-yellow ppt was formed, with m.p =  $134^{\circ}$ C and % yield = 0.241g (71%). On the other hand, concerning Cu(II)/2ABPH complex, the color of solution before precipitation process was faint-yellow and turned to dark-green ppt complex with m.p =  $136^{\circ}$ C, % yield = 0.309 g (97.5%).

#### Microanalytical Techniques

Carbon, hydrogen, and nitrogen contents were determined using a Perkin-Elmer CHN 2400. The copper(II), cobalt(II), and manganese(II) contents were determined gravimetrically by the direct ignition of the complexes at 1000°C for 3 hours till constant weight in the forms of metal oxides.

#### Spectroscopic Investigations

IR spectra were recorded on Bruker FTIR Spectrophotometer  $(4000-400 \text{ cm}^{-1})$  in KBr pellets. The UV–vis, spectra were studied in the DMSO solvent with concentration  $(1.0 \times 10^{-4} \text{ M})$  for the 2-aminobenzaldehyde phenyl hydrazone (2ABPH) and their complexes by help of Jenway 6405 Spectrophotometer with 1cm quartz cell, in the range 800–200 nm. The solid reflectance spectra were performed on a Shimadzu 3101pc spectrophotometer. The purity of ligands and complexes were checked from mass spectra at 70 ev by using AEIMS 30 mass spectrometer with heating rate  $40^{\circ}$ C/min and mass range (50–1000).

Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using Gouy method.

Two very good solid calibrants are used: Hg[Co(CNS)<sub>4</sub>] and [Ni(en)<sub>3</sub>](S<sub>2</sub>O<sub>3</sub>). They are easily prepared pure, do not decompose or absorb moisture, and pack well. Their susceptibilities at  $20^{\circ}$ C are  $16.44 \times 10^{-6}$  and  $11.03 \times 10^{-6}$  c.g.s. units, decreasing by  $0.05 \times 10^{-6}$  and  $0.04 \times 10^{-6}$  per degree temperature raise, respectively, near room temperature. The cobalt compound, besides having the higher susceptibility, also packs rather densely and is suitable for calibrating low fields, while the nickel compound with lower susceptibility and density is suitable for higher field.<sup>[32]</sup> Here we were used Hg[Co(CNS)<sub>4</sub>] only as calibrant.

Molar conductivities of freshly prepared  $1.0 \times 10^{-3}$  mol/dm<sup>-3</sup> DMSO solutions were measured using Jenway 4010 conductivity meter.

Thermogravimetric analysis (TGA and DTG) were carried out in dynamic nitrogen atmosphere (30 ml/min) with a heating rate of 10°C/min using a Schimadzu TGA-50H thermal analyzer.

#### **Optical Absorption**

The absorption spectra were recorded using a perkin-Elmer Lambda 4B spectrophotometer in the range 200–900 nm.



FIG. 2. Spectral emission curves of Xenon arc lamp.

#### **Dye Photostability**

Solar simulator Xenon arc lamp "250 w" was used. The spectrum of lamp is shown in Figure 2, which had the same spectrum as the sun. The degradation of samples was studied by analyzing the UV-vis. absorption spectra. The dye photostability was calculated by dividing the absorbance after exposure to light by that before exposure. The photostability as a function of exposure time has been given.

#### **RESULTS AND DISCUSSION**

The results of the elemental analysis and physical data of the 2-aminobenzaldehyde phenylhydrazone (2ABPH) Schiff base and their Mn(II), Co(II), and Cu(II) complexes exist in Table 1. The complexes are air-stable, with melting points different from the free 2ABPH, insoluble in  $H_2O$ , and most of organic solvents (like alcohols, benzene, acetonitrile) on cold except for DMSO and DMF are very soluble.

#### **Mass Spectra**

The most significant m/z peaks in the Figure 3 of mass spectrum of 2ABPH free ligand were detected and assigned. The 2-aminobenzaldehyde phenylhydrazone (2ABPH) shows one peak at m/z 211 assigned to the  $C_{13}H_{13}N_3$  molecular ion. It also shows a series of peaks, i.e., m/z(%); 195(0.5), 167(3), 105(32), 77(100), and 65(54) corresponding to various fragments;  $[C_{13}H_{11}N_2]^+$ ,  $[C_{12}H_9N]^+$ ,  $[C_7H_7N]^+$ ,  $[C_6H_5]^+$  and  $[C_5H_5]^+$ , respectively. Their signals give an idea about the construction of ligand.

#### **Molar Conductivities of Metal Chelates**

The molar conductivity ( $\Lambda_m$ ) values for the 2ABPH complexes in DMSO solvent ( $1.0 \times 10^{-3}$  M) at 30°C were in the range of (75–81)  $\Omega^{-1}$  cm<sup>-1</sup>M<sup>-1</sup> (Table 1), prove that the presence of coordinated counter ions, since the 2ABPH complexes

TABLE 1
Elemental analyses and physical data of 2-aminobenzaldehyde phenylhydrazone (2ABPH) and their Mn(II), Co(II), and Cu(II)
complexes

			٨			
Complexes	Mwt.	% C	% H	% N	%M	$(\mathrm{S}\mathrm{cm}^2\mathrm{mol}^{-1})$
2ABPH C <sub>13</sub> H <sub>13</sub> N <sub>3</sub>	211.27	(73.84) 73.77	(6.15) 6.13	(19.88) 19.60	_	35
[Mn(2ABPH) <sub>2</sub> (Cl) <sub>2</sub> ].4H <sub>2</sub> O (C <sub>26</sub> H <sub>34</sub> N <sub>6</sub> Cl <sub>2</sub> Mn)	620.48	(50.28) 49.98	(5.48) 5.35	(13.54) 13.48	(8.85) 8.78	77
[Co(2ABPH) <sub>2</sub> (Cl) <sub>2</sub> ].6H <sub>2</sub> O C <sub>26</sub> H <sub>38</sub> N <sub>6</sub> Cl <sub>2</sub> Co)	660.47	(47.24) 47.19	(5.75) 5.66	(12.72) 12.56	(8.92) 8.87	81
$[Cu(2ABPH)_2(Cl)_2].H_2O\ C_{26}H_{28}N_6Cl_2Cu)$	575.09	(54.25) 54.19	(4.87) 4.83	(14.61) 14.45	(11.05) 10.92	75



FIG. 3. Mass spectrum of 2-aminobenzaldehyde phenylhydrazone (2ABPH) ligand.

have a molar ratio (1: 2, M: ligand), and suggesting them to be slightly-electrolytes nature.<sup>[31,33–35]</sup> Conductivity measurements are in a good agreement with the elemental analysis data, where  $Cl^-$  ions are detected by addition of AgNO<sub>3</sub> solution, inside the coordination sphere of the complexes by the dissolving of the all complexes using nitric acid.

#### **Infrared Spectra**

The IR spectra in the (4000–400 cm<sup>-1</sup>) region provide information regarding the coordination mode in the complexes and were analyzed by comparison with data for ligand (2ABPH). The most relevant bands and proposed assignments for all complexes along with the ligand are given in Table 2, and the spectra of ligand and their complexes are shown in Figure 4. The IR spectrum of ligand shows bands at 3424 and 3293 cm<sup>-1</sup>, which may be assigned to the –NH<sub>2</sub>and –NH groups, respectively. In the IR spectra of ligand as well as the complexes, the shifted of band in the region ~3400 cm<sup>-1</sup> corresponding to free primary amine and the blue shift of –CH = N- group towards lower side suggests that the two nitrogen atoms are involved in the complexation process between two moieties of ligand and mononuclear metal(II) chlorides. In the ligand there are three strong intensity bands at 1600, 1572, and 1535 cm<sup>-1</sup> attributable to  $\nu$ (C = N),  $\delta$ (NH<sub>2</sub>) and  $\delta$ (NH), respectively.<sup>[36]</sup> On complexation, the bands corresponding to  $\delta(NH_2)$  and  $\delta(NH)$  are shifted towards lower side (ca. 40-50), which suggest that the ligand acts as bidentate chelating agent coordinating through the lone pair of electron for both nitrogen atoms of -NH<sub>2</sub> and azomethine groups, which is further supported by appearance of a medium intensity band in the region 440–510 cm<sup>-1</sup> assignable to  $\nu$ (M-N) vibration. Bands appearing at 1490, 1442, 1129, 1069, 821, 784, and 745  $cm^{-1}$  are the usual modes of phenyl ring vibrations. The previous bands corresponding to phenyl ring reveal small shifts in the resulted complexes than free ligand; this is usual due to the expected symmetry and electronic structure changes upon complexation.

#### **Electronic Spectra and Magnetic Measurements**

The diffuse reflectance spectrum of the manganese(II) complex shows three bands at 17,482, 22,222, and 27,397 assignable



SCH. 1. Fragment patterns of 2-aminobenzaldehyde phenylhydrazone (2ABPH).

to the  ${}^{4}T_{1g} \rightarrow {}^{6}A_{1g}$ ,  ${}^{4}T_{2g}(G) \rightarrow {}^{6}A_{1g}$  and  ${}^{4}T_{1g}(D) \rightarrow {}^{6}A_{1g}$ , transitions, respectively.<sup>[37]</sup> The magnetic moment value is 5.57 B.M., which proves the presence of Mn(II)/2ABPH complex in octahedral geometry. The electronic spectrum of the cobalt(II)/2ABPH complex have three transition bands located at 15,873, 19,230, and 23,923. These bands are assigned to the  $\nu_1 = {}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F), \ \nu_2 = {}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and  $\nu_3 = {}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(P)$ , respectively. These transitions correspond to the octahedral geometrical structure.<sup>[37]</sup> The magnetic susceptibility measurements at the room temperature were carried out according to Gauy method and lie at 4.45 B.M., indicating the presence of three unpaired electrons.<sup>[38]</sup> Magnetic moment value of copper(II) complex suggests that the Cu(II) complex has octahedral structure with planar arrangement of two ligands molecule around Cu(II)/2ABPH complex and the chloride ions occupying axial position.

The spectra of free ligand 2ABPH and its Mn(II), Co(II), and Cu(II) complexes in DMSO were discussed. There are five essential peaks at around 220 and 500 nm, which are assigned to (220, 245, and 290 nm)  $\pi - \pi^*$  and (340 and 400 nm) n- $\pi^*$  intraligand transitions, respectively. The three bands 220, 245, and 290 nm are probably due to a  $\pi - \pi^*$  of the aromatic rings, but the other two bands 340 and 400 nm are assigned to the azomethine and amino groups.<sup>[39–42]</sup> After complexation, the absorption bands located at the same place of free ligand, but with hyperchromically affected. This mean that the ligand is not deprotonated, but the lone pair of electrons on nitrogen atoms for both -CH = N- and  $NH_2$ -Ph participated in the complexation.

#### **Thermal Analysis**

Thermograms (TG/DTG) of the 2ABPH and their Mn(II), Co(II) and Cu(II) transition metal complexes are discussed and assigned in Table 3 and referred to in Figure 5 as follows.

The 2ABPH ligand melts at about  $227^{\circ}$ C with simultaneous decomposition. The decomposition steps seem to be consistent with a mass loss of (obs. = 98.40%, calc. = 100%) due to evolution of  $13/2C_2H_2+ 3/2N_2$  gaseous molecules. The difference between the calculated and observed data devoted to the residual carbon. From the corresponding DTG curve, only one endothermic peak is noted.

The thermal decomposition of Mn(II)/2ABPH complex occurs within three steps. The first degradation step occurs in the range of 30–250°C, and it is corresponds to the eliminated of 3H<sub>2</sub>O molecules with a weight loss of (obs. = 8.86%, calc. = 8.70%). The second and third steps fall in the range of 250– 800°C, which are assigned to loss of 2HCl + 2C<sub>13</sub>H<sub>13</sub>N<sub>3</sub> with a weight loss (obs = 79.11%, calc = 79.86%). The MnO is the final product remains stable till 800°C.

The thermal decomposition of cobalt(II)/2ABPH complex occurs via four steps. The first step ranged at 30–130°C



 $FIG. \ 4. \quad Infrared \ spectra \ of: \ (A) \ 2ABPH, \ (B) \ Mn^{+2}/2ABPH, \ (C) \ Co^{+2}/2ABPH, \ and \ (D) \ Cu^{+2}/2ABPH.$ 



 TABLE 2

 IR spectral data of the 2ABPH ligand and its complexes

Compounds	$\nu(\mathrm{NH}_2)$	$\nu(NH)$	$\nu(C = N)$	$\delta(\mathrm{NH}_2)$	$\delta(NH)$	ν( <b>M-N</b> )	Phenyl ring
2ABPH	3424	3293	1600	1572	1535		1490
							1442
							1129
							1069
							821
							784
							745
Mn(II)	3419	3295	1595	1530	1489	507 443	1348
							1143
							1068
							808
							750
Co(II)	3405	3297	1595	1527	1491	508	1347
						446	1143
							1097
							1069
							808
							750
Cu(II)	3410	3299	1596	1524	1498	505	1347
							1140
							1096
							1071
							808
							737

corresponding to the loss of  $2H_2O$  molecules representing a weight loss of (obs. = 5.12%, calc. = 5.45%). The second step occurring at 130–200°C assignable to the loss of  $2H_2O$  with a weight loss of (obs. = 6.24%, calc. = 5.45%). The third and fourth steps take place within the temperature range (200–800°C) with the weight loss of (obs. = 69.23%, calc. = 68.58%)

The CoO and the residual carbon atoms are the final products remain stable till  $800^{\circ}$ C.

The thermal degradation of the Cu(II)/2ABPH complex occurs in mainly three degradation stages, reveals a mass loss in the temperature range 30–800°C corresponding to the formation of CuO. The three endothermic peaks were observed in

 TABLE 3

 Kinetic parameters using the Coats–Redfern (CR) and Horowitz–Metzger (HM) operated for 2-aminobenzaldehyde phenylhydrazone (2ABPH) and their Mn(II), Co(II), and Cu(II) complexes

Complex								
	Stage	Method	$\overline{E (\mathrm{kJ}\mathrm{mol}^{-1})}$	$A (s^{-1})$	$\Delta S (\text{J mol}^{-1} \text{ K}^{-1})$	$\Delta H (\mathrm{kJ}\mathrm{mol}^{-1})$	$\Delta G (\mathrm{kJ}\mathrm{mol}^{-1})$	R
2ABPH	1st	CR	$1.20 \times 10^{5}$	$5.12 \times 10^{10}$	$-1.53 \times 10^{1}$	$1.22 \times 10^{5}$	$1.42 \times 10^{4}$	0.9939
		HM	$1.19 \times 10^{5}$	$5.58 \times 10^{10}$	$-1.38 \times 10^{1}$	$1.02 \times 10^{5}$	$1.48 \times 10^{4}$	0.9998
Mn(II)	1st	CR	$1.87 \times 10^{5}$	$1.39 \times 10^{22}$	$-1.78 \times 10^{1}$	$1.62 \times 10^{5}$	$2.00 \times 10^{4}$	0.9890
		HM	$1.80 \times 10^{5}$	$1.54 \times 10^{23}$	$-2.12 \times 10^{1}$	$1.08 \times 10^{5}$	$2.07 \times 10^{4}$	0.9966
Co(II)	1st	CR	$1.31 \times 10^{5}$	$3.65 \times 10^{20}$	$-7.45 \times 10^{1}$	$1.34 \times 10^{5}$	$7.65 \times 10^{4}$	0.9988
		HM	$1.34 \times 10^{5}$	$3.22 \times 10^{20}$	$-8.81 \times 10^{1}$	$1.42 \times 10^{5}$	$7.86 \times 10^{4}$	0.9999
Cu(II)	1st	CR	$1.02 \times 10^{4}$	$4.76 \times 10^{11}$	$-7.63 \times 10^{1}$	$1.96 \times 10^{5}$	$8.46 \times 10^{4}$	0.9958
HM	HM	$1.00 \times 10^{5}$	$5.66 \times 10^{12}$	$-7.84 \times 10^{1}$	$2.81 \times 10^{5}$	$8.66 \times 10^{4}$	0.9939	



FIG. 5. TGA curves of: (A) 2ABPH, (B) Mn<sup>+2</sup>/2ABPH, (C) Co<sup>+2</sup>/2ABPH, and (D) Cu<sup>+2</sup>/2ABPH compounds.

DTG curve (Figure 5). The maxima of these peaks are found to be 245,430, and 550°C, respectively. The mass loss at the first stage in the temperature range 30–250°C corresponds to the melting point of the 2ABPH ligand because no weight loss was detected in the TG curve. The second and third peaks at 430 and 550°C DTG<sub>max</sub>, respectively, correspond to decomposition of the ligand and corresponding to the loss of 2ABPH and 2HCl moieties and the final thermal product obtained at 800°C is CuO. The overall weight loss (obs. = 87.46%, calc. = 86.17%) agrees well with the proposed structure. Based on the essential DTG<sub>max</sub> temperatures of the decomposition of 2aminobenzaldehyde phenylhydrazone complexes, the thermal stabilities of the complexes depend on the central metal ions, the sequence follows:  $Co^{2+}$  (699 °C) >  $Mn^{2+}$  (650°C) >  $Cu^{2+}$ (550°C).

#### **Kinetic Studies**

Most commonly used methods in determining the ratedependent parameters of solid-state non-isothermal decomposition reactions by analysis of TG curves are the differential method of Freeman and Carroll,<sup>[43]</sup> integral method of Coat and Redfern,<sup>[44]</sup> and the approximation method of Horowitz and Metzger.<sup>[45]</sup>

Herein, the general thermal behaviors of the 2ABPH complexes in terms of stability ranges, peak temperatures and values of kinetic parameters, are discussed in Table 4 and Figure 6. The kinetic parameters have been evaluated using the Coats-Redfern equation:

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{(1-\alpha)}^n = \frac{A}{\varphi} \int_{T_1}^{T_2} \exp(-\frac{E^*}{RT}) \mathrm{d}t \qquad [1]$$



FIG. 6. Kinetic data of: (A) 2ABPH, (B) Mn<sup>+2</sup>/2ABPH, (C) Co<sup>+2</sup>/2ABPH, and (D) Cu<sup>+2</sup>/2ABPH compounds.



FIG. 6. (Continued)

This equation on integration gives

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = -\frac{E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right].$$
 [2]

A plot of left-hand side (LHS) against 1/T was drawn.  $E^*$  is the energy of activation in J mol<sup>-1</sup> and calculated from the slop and A in (s<sup>-1</sup>) from the intercept value. The entropy of activation  $\Delta S^*$  in (JK<sup>-1</sup>mol<sup>-1</sup>) was calculated by using the equation:

$$\Delta S^* = R \ln(Ah/k_B T_s), \qquad [3]$$

where  $k_B$  is the Boltzmann constant, h is the Plank's constant and  $T_s$  is the DTG peak temperature.<sup>[46]</sup> The Horowitz-Metzger equation is an illustrative of the approximation methods.

$$\log[\{1 - (1 - \alpha)^{1 - n}\}]/(1 - n)] = E^* \theta / 2.303 RT_s^2 \text{ for } n \neq 1$$
[4]

When n = 1, the LHS of equation 4 would be  $\log[-\log(1-\alpha)]$ . For a first-order kinetic process the Horowitz-Metzger equation may be written in the form:

$$\log[\log(w_{\alpha}/w_{\gamma})] = E^*\theta/2.303RT_s^2 - \log 2.303,$$

where  $\theta = T - T_s$ ,  $w_{\gamma} = w_{\alpha} - w$ ,  $w_{\alpha} = \text{mass loss at the completion of the reaction; } w = \text{mass loss up to time } t$ . The plot of  $\log[\log(w_{\alpha}/w_{\gamma})]$  vs  $\theta$  was drawn and found to be linear

 TABLE 4

 Thermal data of 2-aminobenzaldehyde phenylhydrazone (2ABPH) and their Mn(II), Co(II), and Cu(II) complexes

		Temp. range (°C)	DTG peak (°C)	TGA weight loss (%)			
Compounds	Steps			Calc.	Found	Assignments	
2ABPH	1st	30-800	227	100	98.40	$13/2C_2H_2 + 3/2N_2 + residual carbon$	
Mn(II)	1st	30-250	205	8.70	8.86	3H <sub>2</sub> O	
	2nd , 3rd	250-800	425, 650	79.86	79.11	$2C_{13}H_{13}N_2 + 2HCl$	
						MnO	
Co(II)	1st	30-130	93	5.45	5.12	2H <sub>2</sub> O	
	2nd	130-200	145	5.45	6.24	$2H_2O$	
	3rd, 4th	200-800	435, 699	68.58	69.23	$C_{21}H_{26}N_6$	
						CoO + residual carbon	
Cu(II)	1st	30-800	245			Melting point	
	2nd		430, 550	86.17	87.46	$2C_{13}H_{13}N_2 + 2HCl$	
	3rd					CuO	

Sample	K (m	$nin^{-1}$ )	t <sub>1/2</sub> (mi	t <sub>1/2</sub> (min)				
2ABPH/PMMA	372  nm	275.8  nm	372 nm	275.8 nm				
	$4.807 \times 10^{-4}$	$3.664 \times 10^{-5}$	1441.65	18915				
2ABPH/Mn <sup>2+</sup> complex /PMMA	364.3  nm	274.6  nm	364.3 nm	274.6 nm				
	$3.37 \times 10^{-4}$	$3.357 \times 10^{-5}$	2062	20643				

 TABLE 5

 Rate constants (k) of photodegradation and half life times of doped 2ABPH and their metal complexes in PMMA

from the slope of which  $E^*$  was calculated. The pre-exponential factor, A, was calculated from the following equation:

$$E^*/RT_s^2 = A/[\varphi \exp -E^*/RT_s]$$

The entropy of activation,  $\Delta S^*$ , was calculated from equation 3. The enthalpy activation,  $\Delta H^*$ , and Gibbs free energy,  $\Delta G^*$ , were calculated from;  $\Delta H^* = E^* - RT$  and  $\Delta G^* = \Delta H^* - T\Delta S^*$ , respectively.

 $\Delta G$  is positive for reaction for which  $\Delta H$  is positive and  $\Delta S$  is negative. The reaction for which  $\Delta G$  is positive and  $\Delta S$  is negative considered as unfavorable or non spontaneous reactions.

The thermodynamic data obtained with the two methods are in harmony with each other. The activation energy of  $Mn^{+2}/2ABPH$  complex is expected to increase in relation with decrease in their radii.<sup>[47]</sup> The smaller size of the ions permits a closer approach of the ligand. Hence, the E value for the  $Mn^{+2}$  complex is higher than that for the other Co<sup>+2</sup> and Cu<sup>+2</sup> complexes.

The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to lie in the range 0.98 to 0.99, showing a good fit with linear function. It is clear that the thermal decomposition process of all 2ABPH complexes is non-spontaneous, i.e., the complexes are thermally stable.



FIG. 7. The mode of chelation of the 2ABPH complexes, where M = Mn(II), Co(II), and Cu(II); X = 1, 4 and 6.

#### Structure of the 2ABPH Complexes

It can be concluded from the above discussions on the 2ABPH ligand and its Mn(II), Co(II), and Cu(II) complexes using the elemental analysis, molar conductivity, IR, UV, <sup>1</sup>HNMR, and mass spectra, as well as TG/DTG, that the mode of coordination occurs through both of nitrogen atoms one of them for amino ( $-NH_2$ ) group and the other of lone pair of electron of nitrogen atom specialized to azomethine group (Figure 7).

#### Photostabilities of 2ABPH and their Metal Complexes

In case of 2ABPH undoped, highly delocalized bondes (C=C and C=N) are mainly affected by UV-Vis radiation (photodegradation origin). Also, the photochemical degradation of 2ABPH doped in PMMA occurs only in the presence of suitable optical radiation, which produces large local increases in temperature and thermal destruction of the dye molecules.<sup>[48]</sup> At the Xenon arc lamp powers which are used, there is no general consensus concerning the mechanism responsible for thermal damage of polymeric materials. It can be seen that dye molecules embedded in the PMMA matrix do not undergo any change in chemical properties at low powers.<sup>[48]</sup> 2ABPH doped in PMMA were exposed indoors to UV-Vis radiation and the change in the absorption spectra was achieved at different times during irradiation



FIG. 8. Photostability of 2ABPH doped in PMMA before and after exposure to UV-Vis light. (Figure is provided in color online.)



FIG. 9. Photostability of 2ABPH/ $Mn^{2+}$  complex doped in PMMA before and after exposure to UV-Vis light. (Figure is provided in color online.)

period (230 min and 480 min, respectively) and shown in Figure 8. Also, 2ABPH/Mn<sup>2+</sup> complex was prepared, doped in PMMA, and shown after exposure to UV-Vis radiation an enhancement of the photostability, as shown in Figure 9. The increase in photostability refers to strong chelation (complexation of dye with metal).

The rate constant of photo-degradation of dyes was estimated according to the following equation:<sup>[49]</sup>

$$k = \frac{2.303}{t} \log \frac{A_0}{A}$$
 [5]

Where,  $A_0 \& A$  the absorption before and after irradiation for time (*t*). The *k* value and half life times are listed in Table 5. It is clear from the degradation data that the complexation modifies the photostability of dye.<sup>[50]</sup>

#### REFERENCES

- Knopfer, G. Gegenseitige umsetzung von semicarbazonen und phenylhydrazonen. *Monatsh. Chem.* 1910, 31(2), 87–110.
- Pfeiffer, H. Indirect nitrin test for coli bacilli in the urine. Munch. Med. Wochenschr. 1950, 92(31-32), 1315–1316.
- Selvakumar, P.M.; Suresh, E.; Subramanian, P.S. Synthesis, spectral characterization and structural investigation on some 4-aminoantipyrine containing Schiff base Cu(II) complexes and their molecular association. *Polyhedron* 2007, 26(4), 749–756.
- Boghaei, D.M.; Farvid, S.S.; Gharagozlou, M. Interaction of copper(II) complex of compartmental Schiff base ligand N,N/-bis(3hydroxysalicylidene)ethylenediamine with bovine serum albumin. *Spectrochim. Acta A* 2007, 66(3), 650–655.
- Khanmohammadi, H.; Amani, S.; Lang, H.; Rüeffer, T. Synthesis and characterization of Mg(II), Mn(II), Zn(II) and Cd(II) complexes with a new heptaaza Schiff base pendant-armed macrocycle: X-ray crystal structure, NMR and computational study. *Inorg. Chim. Acta* 2007, 360(2), 579–587.
- Karmakar, R.; Choudhury, C.R.; Batten, S.R.; Mitra, S. Two new copper(II) complexes with the shortest (N–N) diazine based rigid ligand: Example of

unusual tridentate coordination mode. J. Mol. Struct. 2007, 826(2-3), 75-81.

- Patel, R.N.; Singh, N.; Gundla, V.L.N. Synthesis, structure and properties of ternary copper(II) complexes of ONO donor Schiff base, imidazole, 2,2'bipyridine and 1,10-phenanthroline. *Polyhedron* 2006, 25(17), 3312–3318.
- Bortoluzzi, M.; Paolucci, G.; Pitteri, B.; Vavasori, A. Metal-assisted syntheses and NMR characterization of square-planar Pd(II) and Pt(II) complexes with tridentate nitrogen-donor chelate ligands. *Inorg. Chem. Comm.* 2006, 9(12), 1301–1303.
- Banerjee, S.; Lassahn, Paul-G.; Janiak, C.; Ghosh, A. Supramolecular architecture of cadmium(II)–terephthalate complexes having a tridentate or tetradentate Schiff base as blocking coligand. *Polyhedron* 2005, 24(18), 2963–2671.
- Das, S.; Pal, S. Copper(II) complexes with tridentate *N*-(benzoyl)-*N*/-(salicylidine)-hydrazine and monodentate *N*-heterocycles: Investigations of intermolecular interactions in the solid state. *J. Mol. Struct.* 2005, 753(1-3), 68–79.
- Marcos, M.; Barbera, J.; Ros, M. B.; Serrano, J. L. A contribution to the study of the nematic-isotropic transition. influence of polar terminal groups. *Mol. Cryst. Liq. Cryst.* **1988**, *163*, 139–155.
- Marcos, M.; Romero, P.; Serrano, J.L.; Bueno, C.; Cabeza, J.A.; Oro, L.A. Liquid crystal derivatives of transition metals (I): tetracoordinated copper (II) complexes derived from Schiffs bases. *Mol. Cryst. Liq. Cryst.* 1989, 167, 123–134.
- Billman, J.H.; McDowell, J.W. The reductive acylation of Schiff bases using trimethylamine borane. IV. J. Org. Chem. 1962, 27, 2640–2643.
- Metzler, D.E.; Ikawa, M.; Snell, E.E. A general mechanism for vitamin B<sub>6</sub>-catalyzed reactions<sup>1</sup>. J. Am. Chem. Soc. **1954**, 76, 648–652.
- Surati, K.R.; Thaker, B.T. Synthesis, spectral, crystallography and thermal investigations of novel Schiff base complexes of manganese (III) derived from heterocyclic β-diketone with aromatic and aliphatic diamine. *Spectrochim. Acta Part A* 2010, 75(1), 235–242.
- Sridhar, S. K.; Saravanan, M.; Ramesh, A. Synthesis and antibacterial screening of hydrazones, Schiff and Mannich bases of isatin derivatives. *Eur. J. Med. Chem.* 2001, *36*, 615–625.
- Panneerselvam, P.; Nair, R.R.; Vijayalakshmi, G.; Subramanian, E.H.; Sridhar, S.K. Synthesis of Schiff bases of 4-(4-aminophenyl)-morpholine as potential antimicrobial agents. *Eur. J. Med. Chem.* 2005, 40, 225–229.
- Pandeya, S.N.; Sriram, D.; Nath, G.; DeClercq, E. Synthesis, antibacterial, antifungal and anti-HIV activities of Schiff and Mannich bases derived from isatin derivatives and *N*-[4-(4/-chlorophenyl)thiazol-2-yl] thiosemicarbazide. *Eur. J. Pharm. Sci.* **1999**, *9*, 25–31.
- Timmons J. C.; Hubin T.J. Preparations and applications of synthetic linked azamacrocycle ligands and complexes. *Coord. Chem. Rev.* 2010, 254(15-16), 1661–1685.
- Mirkhani, V.; Kia, R.; Vartooni, A.R.; Fun, H.-K. New Re(I) tricarbonyl-diimine complexes with *N*,*N*/-bis(substituted benzaldehyde)-1,2-diiminoethane Schiff base ligands: Synthesis, spectroscopic and electrochemical studies and crystal structures. *Polyhedron* **2010**, *29*(*6*), 1600–1606.
- Jia, L.; Jiang, P.; Xu, J.; Hao, Z.-Y.; Xu, X.-M.; Chen, L.-H.; Wu, J.-C.; Tang, N.; Wang, Q.; Vittal, J.J. Synthesis, crystal structures, DNA-binding properties, cytotoxic and antioxidation activities of several new ternary copper(II) complexes of *N*, *N*/-(*p*-xylylene)di-alanine acid and 1,10-phenanthroline. *Inorg. Chim. Acta* **2010**, *363*(5), 855–865.
- Parker, D.; Dickins, R.S.; Purschmann, H.; Crossland, C.; Howard, J.A.K. Being excited by lanthanide coordination complexes:aqua species, chirality, excited-state chemistry, and exchange dynamics. *Chem. Rev.* 2002, *102*, 1977–2010.
- Parker, D. Excitement in f block: structure, dynamics and function of ninecoordinate chiral lanthanide complexes in aqueous media. *Chem. Soc. Rev.* 2004, 33, 156–165.
- 24. Williams, L.A.D.; Howell, R.C.; Young, R.; Kahwa, I.A. Neuropharmacological actions of some binuclear lanthanide(III) complexes. *Comp.*

Biochem. Physiol. Part C: Toxicol. Pharmacol. 2001, 128, 119–125.

- Woods, M.; Kovacs, Z.; Sherry, A.D. Targeted complexes of lanthanide(III) ions as therapeutic and diagnostic pharmaceuticals. *J. Supramolecular Chem.* 2002, 2, 1–15.
- Refat, M.S.; El-Deen, I. M.; Ibrahim, H.K.; El-Ghool, S. Synthesis and spectroscopic studies of some transition metal complexes of a novel Schiff base ligands derived from 5-phenylazo-salicyladehyde and *o*-amino benzoic acid. *Spectrochim. Acta Part A* 2006, 65(5), 1208–1220.
- Refat, M.S.; Ibrahim, A.A. Synthesis, infrared spectra and thermal studies of Zn(II), Cd(II) and Hg(II) complexes with 2-aminobenzaldehyde phenylhydrazone "nitrin" ligand. *Spectrochim. Acta Part A* 2008, 70(1), 234–242.
- Refat, M.S.; El-Korashy, S.A.; Kumar, Deo N.; Ahmed, A.S. Syntheses and characterization of Ru(III) with chelating containing ONNO donor quadridentate Schiff bases. *Spectrochimica Acta A* 2008, 70(4), 898–906.
- Refat, M.S.; Chandra, S.; Tyagi, M. Spectroscopic, thermal and biocidal studies on Mn(II), Co(II), Ni(II) and Cu(II) complexes of tridentate ligand having semicarbazone moieties. *J. Therm. Anal. Cal.* 2010, 100(1), 261– 267.
- Refat, M.S.; El-Deen, I.M. Grabchev, I.; Anwer, Z.M.; El-Ghol, S. Spectrochim. Acta A. 2009, 72(4), 772.
- Refat, M.S.; El-Deen, I.M.; Anwer, Z.M.; El-Ghol, S. Bivalent transition metal complexes of coumarin-3-yl thiosemicarbazone derivatives: Spectroscopic, antibacterial activity and thermogravimetric studies. *J. Mol. Str.* 2009, 920, 149–162.
- Burger, K. Coordination Chemistry: Experimental Methods; Butterworth group: Britain, 1973.
- Geary, W.J. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coord. Chem. Rev.* 1971, 7, 81–122.
- Abd El-Wahed, M.G.; Refat, M.S.; El-Megharbel, S.M. Spectroscopic studies on the complexation of some transition metals with Chloramphenicol drug. J. Mol. Str. 2008, 892(1-3), 402–413.
- Refat, M.S.; El-Deen, I.M.; Anwer, Z.M.; El-Ghol, S. Spectroscopic studies and biological evaluation of some transition metal complexes of Schiff-base ligands derived from 5-arylazo-salicylaldehyde and thiosemicarbazide. *J. Coord. Chem.* 2009, 62(10), 1709–1718.
- Nakamoto, K. Infrared Spectra of Inorganic and Coordination Compounds; Wiley Interscience: NY, 1970.

- Lever, A.B.P. Inorganic Electronic Spectroscopy, 1st Ed.; Elsevier: Amsterdam, 1968.
- Earnshaw, A. Introduction to Magneto Chemistry; Academic press Inc.: 1968.
- Fasman, G.D. Handbook of Biochemistry and Molecular Biology; Nucleic Acids, I, 65–215, CRC Press, 1968.
- Kasumov, V.T.; Ozalp-Yaman, S.; Tas, E. Synthesis, spectroscopy and electrochemical behaviors of nickel(II) complexes with tetradentate Shiff bases derived from 3,5-Bu<sup>t</sup><sub>2</sub>-salicylaldehyde. *Spectrochimica Acta A* 2005, *62*, 716–720.
- Zollezi, S.; Decinti, A.; Spodine, E. Syntheses and characterization of copper(II) complexes with Schiff-base ligands derived from ethylenediamine, diphenylethylenediamine and nitro, bromo and methoxy salicylaldehyde. *Polyhedron* 1999, 18, 897–904.
- Tuncel, M.; Serin, S. Synthesis and characterization of Copper(II), Nickel(II) and Cobalt(II) complexes with Azo-linked Schiff base ligands. Synth. React. Inorg. Met.-Org. Nano Met. Chem. 2005, 35, 203–212.
- Freeman, E.S.; Carroll, B. The application of thermoanalytical techniques to reaction kinetics: the thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate. *J. Phys. Chem.* **1958**, *62*, 394–397.
- Coats, A.W.; Redfern, J.P. Kinetic parameters from thermogravimetric data. Nature 1964, 201, 68–9.
- Horowitz, H.W.; Metzger, G. A new analysis of thermogravimetric traces. Anal. Chem. 1963, 35, 1464–8.
- Flynn, J.H.; Wall, L.A. A quick, direct method for the determination of activation energy from thermogravimetric data. *Polym. Lett.* **1966**, *4*, 323– 8.
- Tunali, N.K.; Ozkar, S. *Inorganic Chemistry*; Gazi University Publication, Pub. No. 185, AnKara, 1993.
- Kim, O.; Lee, K.; Huang, Z.; Heuer, W.; Paik-Sung, C. Oligothiophene as photonic/electronic property modulator. *Optical Materials* 2003, 21, 559– 564.
- Grabchev, I.; Bojinov, V. Synthesis and characterisation of fluorescent polyacrylonitrile copolymers with 1,8-naphthalimide side chains. *Polym. Degrad. Stab.* 2000, 70(2), 147–153.
- Esumi, K.; Hayakawa, K.; Yoshimura, T. Morphological change of gold– dendrimer nanocomposites by laser irradiation. *J. Colloid and Interface Science* 2003, 268(2), 501–6.