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To cite this article: Wail Al Zoubi, Abbas Ali Salih Al-Hamdani & Young Gun Ko (2017) Schiff bases and their complexes: Recent progress in thermal analysis, Separation Science and Technology, 52:6, 1052-1069, DOI: [10.1080/01496395.2016.1267756](https://doi.org/10.1080/01496395.2016.1267756)

To link to this article: <http://dx.doi.org/10.1080/01496395.2016.1267756>



Accepted author version posted online: 09 Dec 2016.
Published online: 09 Dec 2016.



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Schiff bases and their complexes: Recent progress in thermal analysis

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ABSTRACT

Schiff bases are versatile compounds synthesized from the condensation of primary amino compounds with aldehydes or ketones. The high thermal of many Schiff base and their complexes were useful attributes for their application as catalysts in reactions involving at high temperatures. This thermal behavior of Schiff bases and their complexes was evaluated by TGA/DTG and DTA curves with mass losses related to dehydration and decomposition. This review summarizes the developments in the last decade for thermal analysis of Schiff bases. Therefore, synthesis of Schiff bases and their complexes are reviewed.

ARTICLE HISTORY

Received 11 June 2016
Accepted 29 November 2016

KEYWORDS

Carbonyl compound; complexes; imines; Schiff bases; thermal analysis

Introduction

Compounds containing an azomethine group (CH=N), known as Schiff bases, were formed by the condensation of a primary amine with a carbonyl compound. Schiff bases of aliphatic aldehydes were relatively unstable and were readily polymerizable, while those of aromatic aldehydes, having an effective conjugation system, were more stable. In addition, Schiff bases have a number of applications such as preparative use, identification, and determination of aldehydes or ketones, purification of carbonyl or amino compounds, or protection of these groups during complex or sensitive reaction.

Schiff bases were generally bi- or tri-dentate ligands capable of forming very stable complexes with transition metals. In organic synthesis, Schiff base reactions were useful in making carbon–nitrogen bonds. In this review, we will study the synthesis and the thermal analysis of Schiff bases and their complexes.^[1]

Thermal analysis of Schiff bases and their complexes

Hamid et al.^[2] have synthesized five pyridazine-based azo (Fig. 1) chromophores by the condensation reaction of 3,6-bis ((aminoethyl)thio)pyridazine with 5-(4-X-phenyl)-azo-salicylaldehyde (X=NO₂, Cl, and Et), 5-(2,4-di-Cl-phenyl)azo-salicylaldehyde, and 5-(3,4-di-Cl-phenyl)-azo-salicylaldehyde. These compounds were characterized by elemental analysis, thermal analyses, infrared (IR) spectroscopy, ultraviolet–visible spectroscopy (UV–Vis), nuclear magnetic resonance (NMR) spectrometry,

and mass spectroscopy. Spectral characteristics of the prepared compounds were investigated in four organic solvents of different polarity; thermal studies indicate that the framework of compounds was stable up to 220°C. Complexation of the azo compounds with Cu (II) gave subtle changes in their absorption spectra. In addition, the results indicated that the UV–Vis spectra of these compounds were dependent on solvent polarity. On the other hand, the results of thermal analysis indicated that the 4-nitro and 4-ethyl containing compounds were stable than the others.

Aranha et al.^[3] have reported the synthesis and characteristics of several Schiff bases (Fig. 2) coordinated to vanadyl, VO (Schiff base) by thermogravimetric analysis (TGA) in order to evaluate their thermal stability and thermal decomposition pathways. The number of decomposition steps of the ligand depends on the substituent group and the steric of ligands. The intermediates of the thermal decomposition processes were characterized by their IR spectra. In addition, the results indicated that the thermal stability for ligands is as follows: t-Salcn < 4-OH-t-Salcn < 4-DEA-tSalcn and for the complexes is [VO (4-OH-t-Salcn)].H₂O < [VO (4-DEA-t-Salcn)] < [VO (t-Salcn)].

Larisa et al.^[4] have reported the synthesis of Schiff base derived from acetylacetone and 3-amino-4H-1,2,4-triazole by template condensation. The characterization of complexes (Fig. 3) has been assigned from microanalytical, IR, and UV–Vis–NIR data. Thermal decomposition of Schiff bases complexes allowed establishing the number and nature of water molecules, and the composition of complexes.

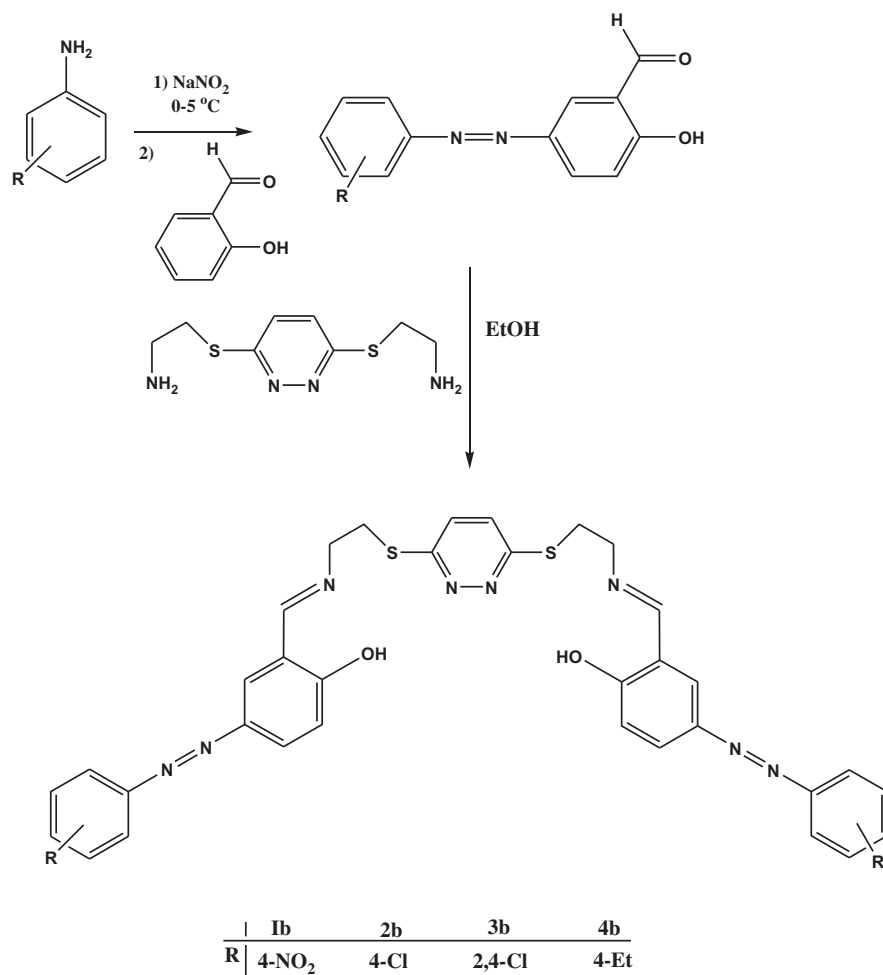


Figure 1. Azo-linked pyridazine-based ligands.

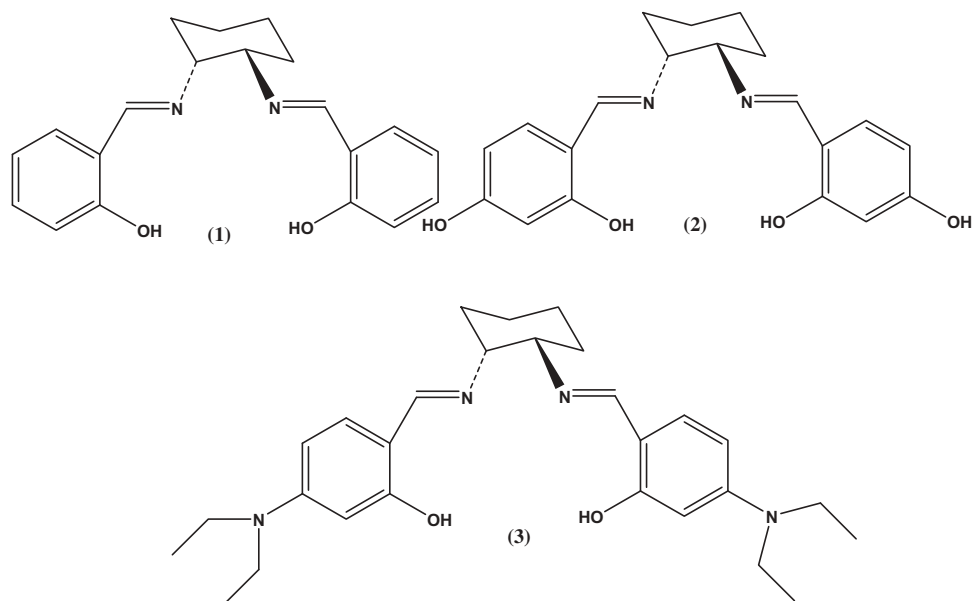


Figure 2. Structural representations of the ligands and complexes: (1) t-Salcn, (2) 4-OH-t-salcn, and (3) 4-EDA-t-Salcn.

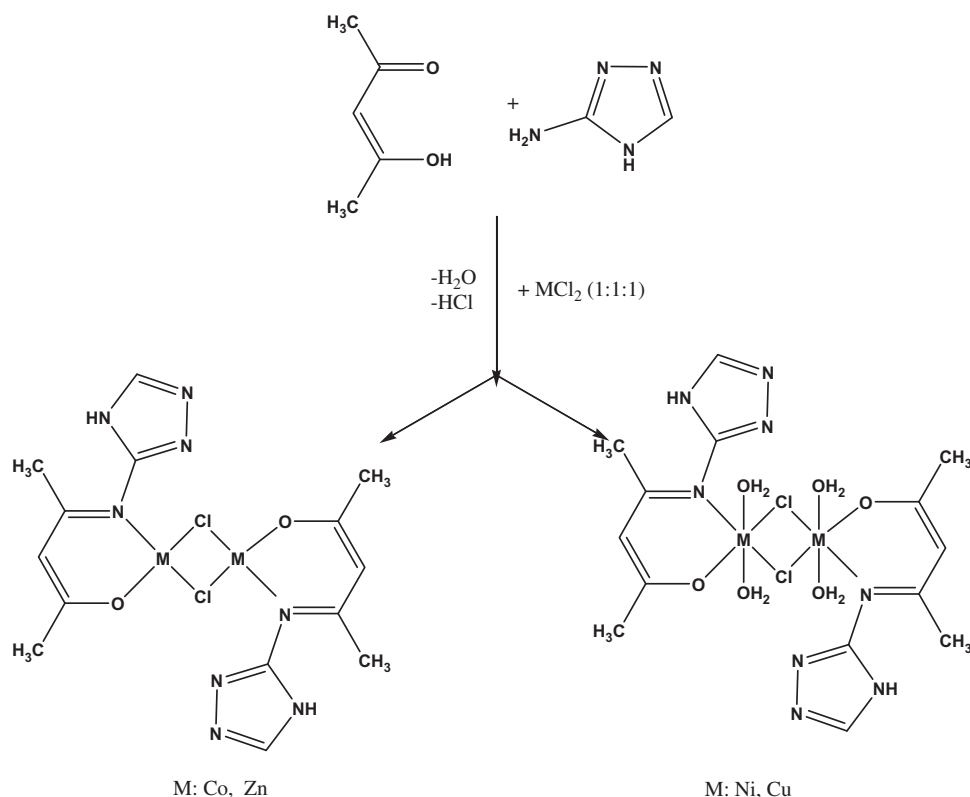


Figure 3. Synthetic route to prepare complexes and coordination proposed.

The water molecule elimination in one or two well-defined events was observed for hydrated complexes. The second step corresponds to chloride anion removal as hydrochloric acid. Therefore, Schiff base complexes decomposed in one or two steps leading to metal oxide as residue. In addition, the anhydrous (non-water) complexes melt before the thermal decomposition start.

Schiff base (L) ligand was prepared via condensation of pyridine-2,6-dicarboxaldehyde with aminopyridine. The ligand and its metal complexes were characterized based on elemental analysis, mass, IR, solid reflectance, magnetic moment, molar conductance, and thermal analyses (TGA, DTG, and DTA). The thermal behavior of these chelates showed that the hydrated complexes losses water molecules of hydration in the first step followed immediately by decomposition of the anions, and ligand molecules in the subsequent steps. The activation thermodynamic parameters, such as E , ΔH , ΔS , and ΔG , were calculated from the derivative thermogravimetric (DTG) curves by using the Coats–Redfern method.^[5]

Kelode et al.^[6] have reported the synthesis and characteristics of Schiff base complexes of Co(II), Ni(II), Cu(II), Zn(II), Cr(III), Fe(III), Mn(III), VO(IV), and Zr(IV) with Schiff base [LH₂] (Fig. 4) derived from 2,4-dihydroxy benzophenone and isonicotinoyl hydrazide on the basis of elemental analysis, IR, ¹H NMR, molar conductance, magnetic susceptibilities, electronic spectra, and TGA.

The analysis of magnetic susceptibility, thermal analysis, and electronic spectral data indicated square planar geometry for the Cu(II) and Ni(II) complexes, square pyramidal geometry for the Mn(II) and VO(IV) complexes, and octahedral geometry for the other complexes.

Chavan et al. have reported the Schiff base (Fig. 5) synthesized using 2-hydroxy-1-naphthaldehyde and o-phenylene diamine to synthesize Ru(II), Rh(III), and Pd(II) complexes using 1:1 metal: ligand stoichiometric proportion. The structures of Schiff base and metal complexes were proposed on the basis of elemental analysis, molar conductivity, magnetic susceptibility, and various analytical techniques, such as UV–Vis, IR spectroscopy, ¹H NMR spectrometry, X-ray powder diffraction (XRD), and thermal analysis. Ru(III) and Rh(III) complexes may exhibited octahedral geometries and Pd(II) complex may exhibited square planar geometry, whereas the Schiff base was appeared as tetradentate ligand. TGA/DTA of Ru(III) and Rh(III) complexes have shown a significant loss in weight in the temperature range 20°C–250°C. This observation suggests the presence of water of crystallization as well as coordinated water. TGA/DTA of Ru(III) and Rh(III) complexes have shown a significant loss in weight in the temperature range 20°C–250°C, whereas Pd(II) complex have not shown any weight loss in the temperature range 30°C–250°C, indicating the absence of lattice water as well as coordinated water.^[7]

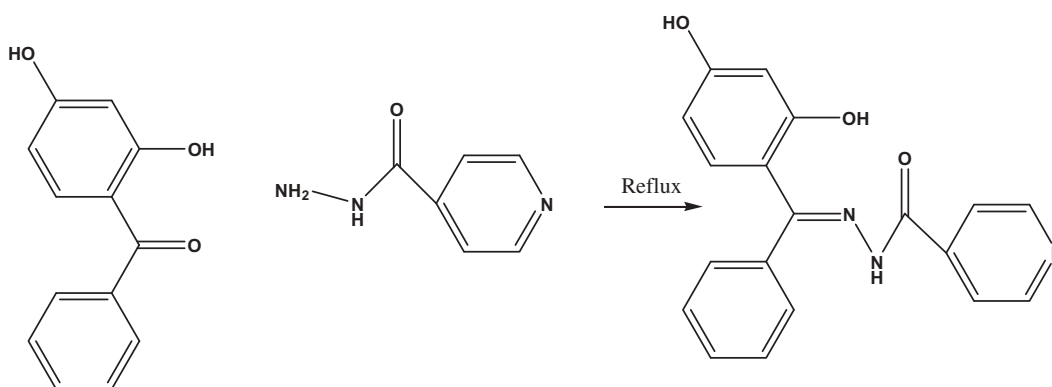


Figure 4. Synthesis of the ligand (LH_2).

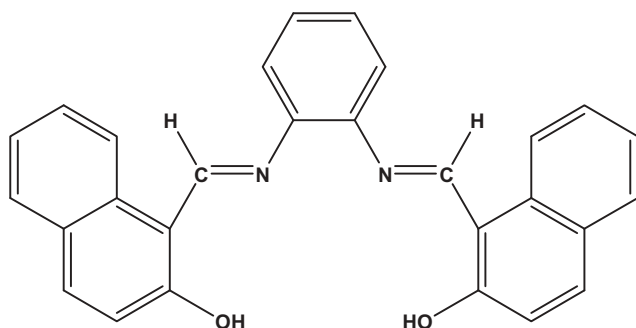


Figure 5. Structure of Schiff base prepared from 2-hydroxy-1-naphthaldehyde and *o*-phenylene diamine.

Cristovao et al.^[8] synthesized and characterized mononuclear Cu(II) and Ni(II) complexes of the formulae $[Cu(L^1)]$, $[(Ni(L^1))_2]$, $[Cu(L^2)H_2O]$, and $[Cu(L^3)]$ (where $L^1=N,N'$ -ethylenebis(4,6-dimethoxysalicylideneamino), $L^2=N,N'$ -ethylenebis(5-bromosalicylideneamino), and $L^3=N,N'$ -ethylenebis(5-bromo-3-methoxysalicylideneamino)) as microcrystalline powders by IR spectroscopy, thermal analysis, and magnetic measurements. In addition, thermal analyses showed no mass up to 300 and 290°C, respectively, indicating the absence of water molecules and other adsorbed solvent molecules in coordination sphere.

TGA has been used to investigate the thermal decomposition kinetics of Cl-, Br-, and acetate complexes of 2-phenyl-1,2,3-triazole-4-carboxalideneaniline with Cu(II). The decomposition process consisted of two stages for all the complexes. Kinetic parameters were evaluated using the Coats–Redfern equation. Furthermore, the results of the kinetic study have been correlated with the catalytic activity of these complexes in the oxidation of hydroquinone with dioxygen. On the other hand, it is worth mentioning that the increasing order of catalytic activity (bromo complex > chloro complex > acetate complex) of these complexes was the same as their decreasing order of activation entropy for the first stage of thermal decomposition. Thus, the catalytic

studies further strengthen our suggestion that the decrease in ΔS values for the first stage was mainly due to oxygen chemisorption.^[9]

Kiran Singh and coworkers have reported the synthesis and characteristics of two new heterocyclic Schiff bases (Fig. 6) of 4-amino-5-mercapto-3-H/propyl-1,2,4-triazole and 5-nitrofurfuraldehyde [HL] and their Co (II), Ni(II), Cu(II), and Zn(II) complexes by elemental analyses, spectral analysis, and thermal techniques. The results showed that the thermogravimetric curve of Ni (L^1)₂·2H₂O consisted mainly of three steps in the temperature range 5–190, 190–424, and 424–750 °C. Therefore, the decomposition of all the complexes ended with oxide formation.^[10]

Montazerzohori et al.^[11] have reported the synthesis, spectroscopic, and thermal studies of some complexes of a new N₂-Schiff base ligand of N₁,N₂-bis((E)-2-methyl-3-phenylallylidene)ethane-1,2-diamine (L) with a general formula of MLX_2 (M=Zn(II), Cd(II), and Hg(II); X = Cl⁻, Br⁻, I⁻, SCN⁻, and N₃⁻) (Fig. 7). The thermal behavior of the complexes showed mass loss by decomposition of the anions and ligand segments in the subsequent steps. Some activation thermodynamic parameters such as E , ΔH , ΔS , and ΔG were calculated from thermal analysis. In other complexes, weight loss was not observed until the temperature reached to 200°C, indicating no water molecule (as lattice water or coordinated) in the compounds.

Sadeek and coworkers have reported the synthesis of the Schiff base complexes (Fig. 8) of Pb(II) and Sn(II) with bidentate (NO), $[M(\text{sal-An})_2]$ (sal-An=aniline salicylideneiminato); tridentate (ONO), $[M(\text{sal-OAP})H_2O]$ (sal-OAP = ortho-aminophenol salicylideneiminato); and tetradentate (N₂O₂) $[M(\text{sal-o-phdn})]$ (sal-o-phdn=N,N'-*o*-phenylene bis(salicylideneiminato)). In addition, DTA and TGA for all complexes were also carried out. The data obtained indicate that the complexes of both bi- and tetradentate ligands were

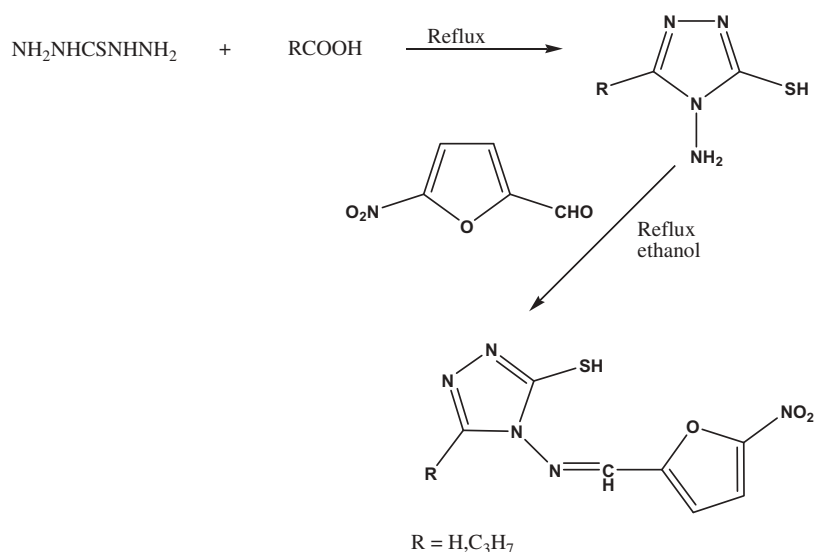


Figure 6. Scheme for the syntheses of Schiff bases.

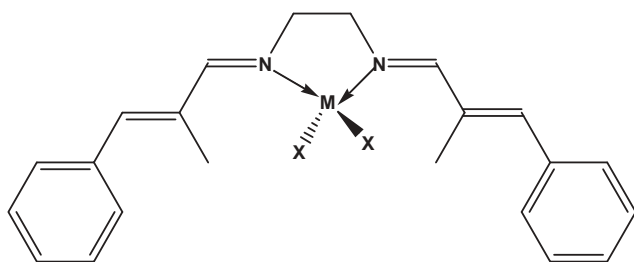


Figure 7. The structure of Schiff base complexes (M=Zn(II), Cd(II), Hg(II); X=Cl⁻, Br⁻, I⁻, SCN⁻, and N₃⁻).

decomposed in one stage, but the complexes of tridentate were decomposed in two steps.^[12]

Sahebalzamani and coworker have reported the synthesis number of new complexes by reaction of novel ligands (Fig. 9) acetic acid (2-hydroxy-benzylidene)-hydrazide (L) with mercury (II) halide. The

structure of the complexes obtained was characterized based on elemental analysis and thermal analyses. In addition, TGA-DTA and other analytical methods have been applied to the investigation of the thermal behavior and structure of the compounds [Hg(L)₂]Cl₂. The thermal decomposition of these compounds was multistage processes.^[13]

Gaurav et al.^[14] have reported the preparation of new unsymmetrical Schiff base ligand (H₂L) (Fig. 10) via condensation of 2-hydroxy-5-methyl acetophenone, 2-hydroxy-5-chloro-3-nitro acetophenone and carbohydrazide in 1:1:1 ratio. Metal complexes of VO(IV), Cr(III), Mn(III), Fe(III), Zr(IV), Mo(VI), WO(VI), and UO(VI) have been prepared. These complexes were characterized by elemental analysis. However, the obtained results indicated that these complexes were found to be quite stable and their thermal decomposition was generally via

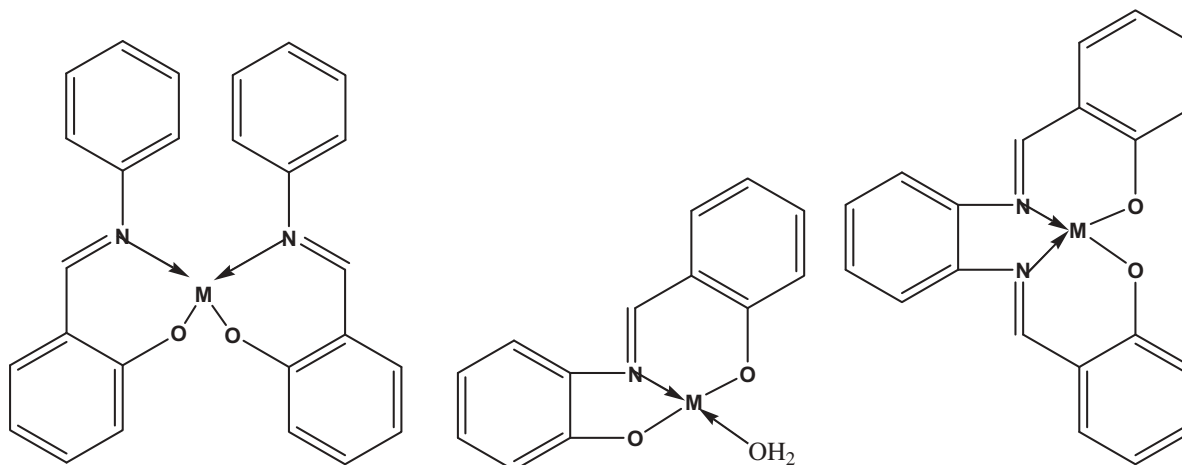


Figure 8. Scheme representations of complexes of Schiff bases.

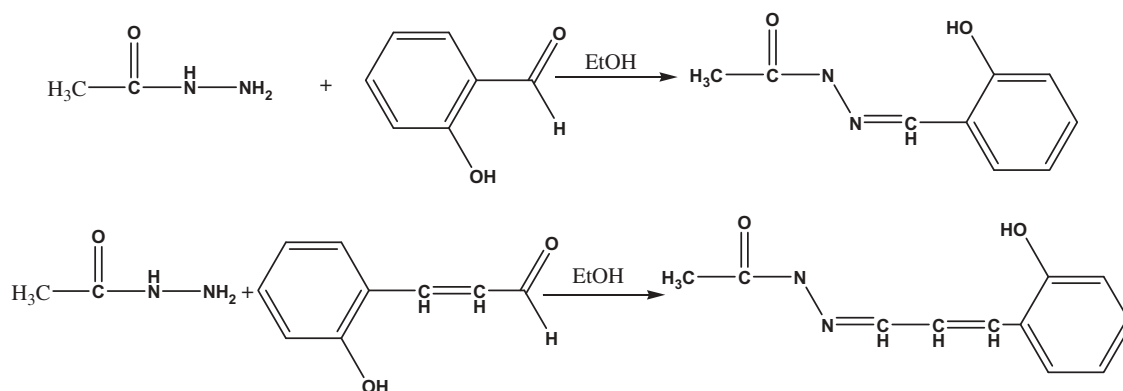


Figure 9. Schematic representation of ligands formation of compounds.

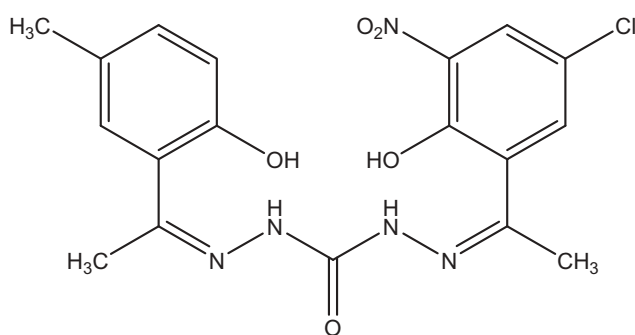


Figure 10. Structure of the Schiff base (H_2L).

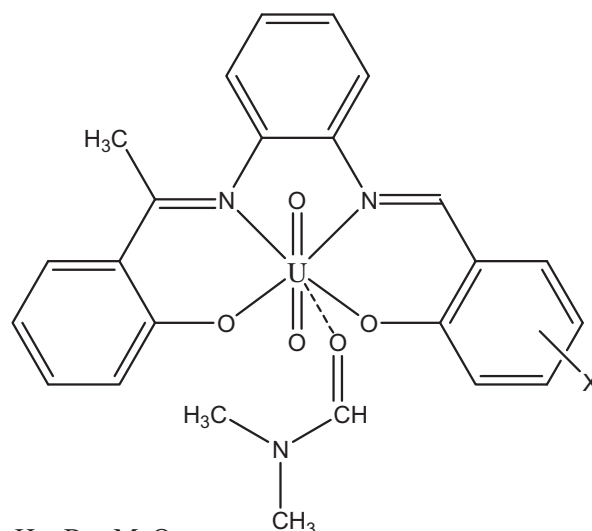
partially loss of the organic moiety and ended with respective metal oxide as a final product. In addition, the element analysis showed 1:1 metal-to-ligand stoichiometry for the previous complexes.

On the other hand, new tridentate ligand 3-amino-4-[1,5-dimethyl-3-[2-(5-methyl-1H-indol-3-yl)-ethylimino]-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylazo]-phenol L was synthesized from the reaction of 1,5-dimethyl-3-[2-(5-methyl-1H-indol-3-yl)-ethylimino]-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamine and 3,4-amino phenol. In addition, complexes of these ligand $[Ni(II)(L)(H_2O)_2Cl]Cl$, $[Pt(IV)(L)Cl_3]Cl$, and $[M(II)(L)Cl]Cl$ ($M = Pd(II), Zn(II), Cd(II), \text{ and } Hg(II)$) were synthesized. The studies revealed octahedral geometries for Ni(II) and Pt(IV) complexes, square planar geometry for Pd(II) complex, and tetrahedral geometry for Zn(II), Cd(II), and Hg(II) complexes. The thermodynamic parameters for these complexes were calculated from the TGA curve by using the Coats–Redfern method.^[15]

Kianfar et al.^[16] have synthesized and characterized the new uranyl complexes with tetradentate unsymmetrical N_2O_2 Schiff base ligands (Fig. 11) by IR, UV–Vis, NMR, and elemental analysis. TGA and DTA of the uranyl complexes were carried out in the temperature range of 20°C–700°C. In this study, they found that the

UO_2L^1 complex was decomposed in two steps and the other complexes were decomposed in three steps. Up to 100°C, the coordinated solvent was released, and then the Schiff base ligands were decomposed in one or two steps. However, the thermal decomposition reaction was of the first order for the studied complex. Moreover, the complex containing simple ligand was decomposed in two steps, while the other complexes containing functional groups were decomposed in three steps. On the other hand, the thermal decomposition pathways of the complexes were related to the Schiff base characteristics.^[16]

Azo group-containing Schiff base ligands (Fig. 12), namely 1-{3-[(3-hydroxypropylimino) methyl]-4-hydroxyphenylazo}-4-nitrobenzene, 1-{3-[(3-hydroxypropylimino) methyl]-4-hydroxyphenylazo}-2-chloro-4-nitrobenzene, and 1-{3-[(3-hydroxypropylimino) methyl]-4-hydroxyphenylazo}-4-chloro-3-nitrobenzene were synthesized. Next, the corresponding copper(II) and cobalt(II) metal



X = H, Br, MeO

Figure 11. The structure of uranyl complexes.

complexes were synthesized and characterized by the physicochemical and spectroscopic methods of elemental analysis, Fourier transform infrared spectroscopy (FTIR), UV-Vis, magnetic moment measurements, and TGA, and differential scanning calorimetry (DSC). The results indicated that the copper complexes were more thermally stable than the azo dye ligand; moreover, the decompositions of the copper complexes all ended with formation of CuO. In addition, metal complexes derived from salicylideneamine were among the best-known classes of metallomesogens.^[17] In the recent years, Schiff base (N_2O_2) containing nitrogen-oxygen atoms was designed and synthesized by the reaction of 5-amino-2-methoxy-phenol with terephthalaldehyde for the best studies in the thermal analysis.^[18]

The VO(IV) complexes of tridentate ONN Schiff ligands (Fig. 13) were synthesized and characterized by IR, UV-Vis, and elemental analysis. TGA and DTA of the VO(IV) complexes were carried out in the temperature range of 20°C–700°C. The $VOL^1(OH_2)$ and $VOL^2(OH_2)$ complexes decomposed in three steps, whereas the $VOL^3(OH_2)$ and $VOL^4(OH_2)$ complexes decomposed in two steps. The thermal decomposition of these complexes was closely related to the nature of the Schiff base ligands and proceeds via the first-order kinetics. Moreover, the results showed that the complexes containing simple ONN and methoxy functional group ligand were decomposed in three steps and the complexes containing Br and NO_2 functional groups were decomposed in two steps.^[19]

Kianfar et al. have reported the synthesis and characterization of some new tridentate ONO and ONS Schiff base (Fig. 14) complexes of $[NiL(amine)]$ (L =Salicylidene-2-aminophenol and Salicylidene-2-

aminothiophenol, amine=benzylamine, morpholine, pyrrolidine and piperidine) by IR, UV, 1H NMR spectroscopy, and elemental analysis. TGA and DTA of the synthesized complexes were carried out in the temperature range of 20°C–700°C, leading to decomposition of ONO type in two stages and ONS type in three stages; moreover, the ONO complexes decomposed to NiO, while the ONS complexes decomposed to NiS. In addition, thermal decomposition of the complexes was closely related to the nature of the Schiff base ligands and proceeds via the first-order kinetics.^[20]

Kianfar and coworkers have reported the synthesis and characterization of the new $[UO_2L(CH_3OH)]$ [where L =bis(salicylaldehyde)-2,6-diiminopyridine (L^1), bis(5-methoxysalicylaldehyde)-2,6-diiminopyridine (L^2), bis(5-bromosalicylaldehyde)-2,6-diiminopyridine (L^3), and bis(5-nitrosalicylaldehyde)-2,6-diiminopyridine (L^4)] complexes by IR, UV-Vis, and elemental analysis. TGA and DTA of the uranyl complexes were carried out in the temperature range of 20°C–700°C. The complex containing simple ligand (L^4) was decomposed in two steps and the other complexes were decomposed in three steps. Up to 85°C, the coordinated solvent was released, then the Schiff base ligands were decomposed in one or two steps. On the other hand, the decomposition of synthesized complexes was related to the Schiff base characteristics. In addition, the thermal decomposition pathways of the complexes were related to the Schiff base properties. Thermal decomposition reaction was first order for the studied complexes.^[21]

Tetradentate N_2O_2 , N_4 Schiff bases, 1,2-bis(4-oxopent-2-ylideneamino) benzene (BOAB), 1-(4-oxopent-2-ylideneamino-2-[(2-hydroxyphenyl)ethylideneamino]

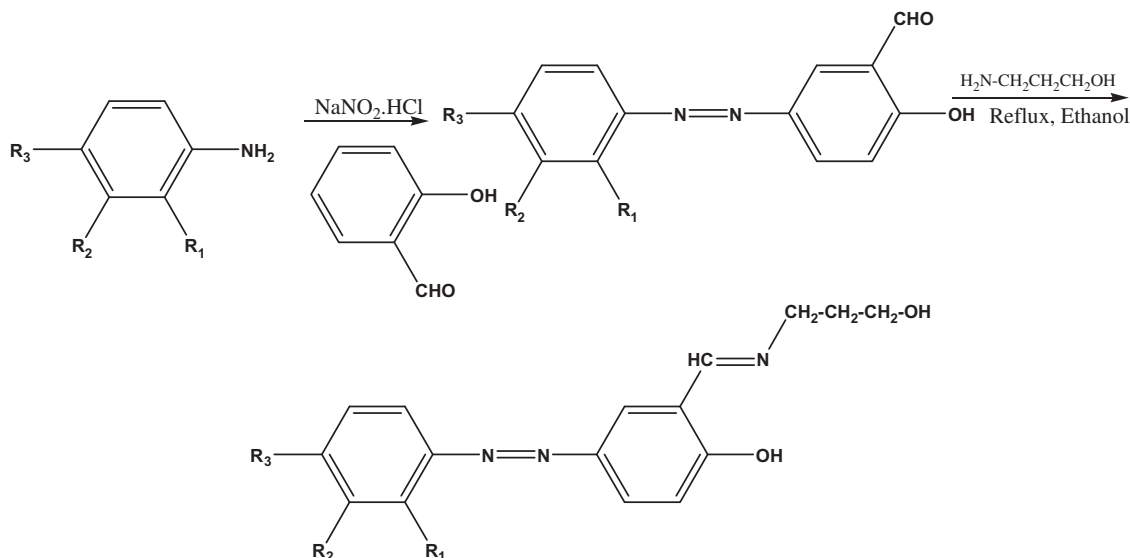


Figure 12. Preparation of Schiff base Ligands.

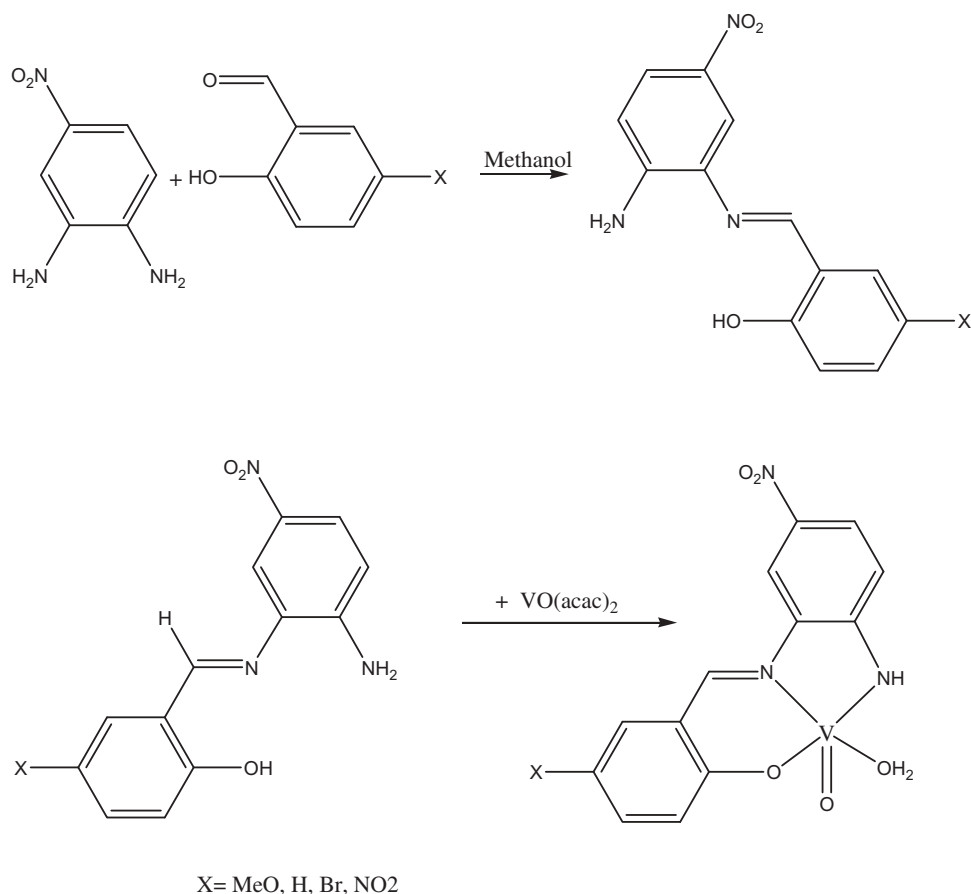


Figure 13. The structure of Schiff base ligand and vanadyl complexes.

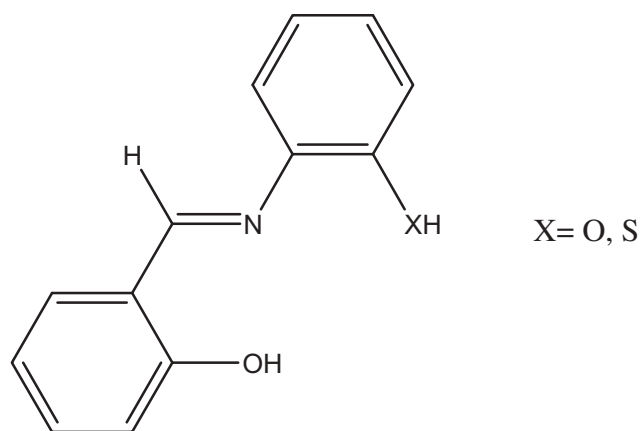


Figure 14. The structure of Schiff base ligands.

benzene (OAHAB), 7.16-bis(4-chlorobenzylidene)-6.8.15.17-tetra-methyl-7.16-dihydro-5,9,14,18-tetraza-dibenzocyclo tetradecene (BCBDCT), 7.16-bis(2-hydroxy-benzylidene)-6.8.15.17-tetramethyl-7.16-dihydro-5.9.14.18-tetraza-dibenzo[a,h] cyclotetradecene (BHBDCT) and hexadentate N₄O₂ Schiff bases, 2,4-bis {2-[1-(2-hydroxyphenyl) ethylideneamino] phenylimino}-3-(2-hydroxybenzylidene) pentane (BHAPHP),

and 2,4-bis {2-[1-(2-hydroxyphenyl)ethylideneamino] phenylimino}-3-(4-chlorobenzylidene) pentane (BHAPCP) (Fig. 15) were prepared and characterized by elemental analysis, IR, UV-Vis, ¹H NMR, and mass spectra. The results showed that the TGA suggested high stability for most complexes followed by thermal decomposition in different steps. In addition, the kinetic and thermodynamic parameters for decomposition steps in Cu (II) complexes thermograms have been calculated.^[22]

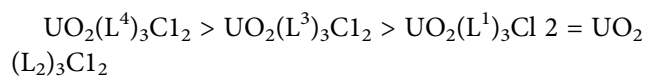
Nihal et al. have reported the preparation and characterization of the Schiff base ligands and their Cu(II), Co (II), Ni(II), Fe(III), Ru(III), and VO(IV) complexes by spectroscopic and analytical techniques. Keto-enol tautomeric forms of the ligands have been investigated in non-polar and polar solvents. Thermal properties of the complexes have been assessed using thermal techniques and similar properties were found. First, in the Fe(II) and Ru (II) complexes, the coordinated water molecules were lost from the complex; in the second step, the chloride ions left the molecules in the temperature range of 300°C–350°C. Finally, the complexes decompose to the metal oxide at the higher temperature ranges. The electrochemical properties of the complexes have been studied in two different solvents (DMF and CH₃CN).^[23]

to fall into one of two categories, e.g., $\text{Bu}_2\text{SnL(I)}$ complexes that decompose without melting to give SnO . The mathematical analysis of TGA data using Coats–Redfern equation, Horowitz–Metzger equation, and Fuoss method showed that the first-order kinetics was applicable in all the complexes except $\text{Bu}_2\text{SnL-2(II)}$. The kinetic parameters such as the energy and entropy of activation and pre-exponential factor are reported.^[24]

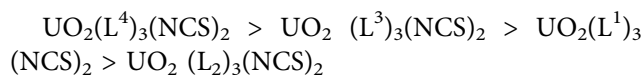
A new unsymmetrical solid Schiff base (LLi) was synthesized using L-lysine, salicylaldehyde, and furfural. The solid lanthanum (III) complex of this ligand $[\text{LaL}(\text{NO}_3)]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ has been prepared and characterized by elemental analyses, IR, UV, and molar conductance. The thermal decomposition kinetics of the complex for the second stage was studied under nonisothermal condition by TGA and DTG methods. The kinetic equation can be expressed as $da/dt = Ae^{-E/RT} \cdot (1-a)^2 \gamma$. The activation thermodynamic parameters, such as, ΔA^* , ΔS^* and ΔG^* were calculated from the TG curves using Coats–Redfern method. In addition, the results in this work indicated that L-lysine can react with salicylaldehyde and furfural-forming unsymmetrical Schiff base LLi and lanthanum nitrate can form stable solid complex with this ligand.^[25, 26]

Panda et al. have reported the preparation of the bidentate Schiff base ligand (NO), furfurylidene arylamine(L), by reaction in situ of furfural and aromatic amine(1:1) in EtOH, reacted with UO_2X_2 ($\text{X} = \text{Cl}, \text{NCS}$) to form red, diamagnetic complexes of the type $[\text{UO}_2(\text{L})_3\text{X}_2]$, which are nonelectrolytic and 10-coordinated. All these complexes remain thermally stable at least up to ca. 150°C and thereafter lose the ligand molecules in several steps finally forming U_3O_8 above 750°C – 800°C . Schiff base (L) ligand was prepared via condensation of pyridine-2,6-dicrboxaldehyde with 2-aminopyridine. This ligand and its complexes were characterized based on elemental analysis, mass, IR, solid reflectance, magnetic moment, molar conductance, and thermal analyses (TGA, DTG, and DTA). The activation thermodynamic parameters, such as ΔE^* , ΔH^* , ΔS^* , and ΔG^* , are calculated from the DTG curves by using the Coats–Redfern method. On the other hand, all complexes in this work were found to be exceptionally stable at room temperature, where they can be kept unchanged for a prolonged period. In addition, the following order of stability for the chloro and isothiocyanato complexes of $\text{UO}_2(\text{VI})$ with furfural-based Schiff bases were established^[27]:

chloro complexes



isothiocyanato complexes



Abdel-Fattah and coworkers have reported the synthesis of several new complexes of Schiff base ligands (Fig. 16) with transition metal ions, such as Cr(III), Fe(III), Co(II), and Zn(II). The thermal decomposition of complexes was found to be the first-order reaction and the thermodynamic parameters corresponding to the different decomposition steps were reported. In addition, the results indicated that the thermal behavior of these chelates showed that the hydrated complexes lose water molecules of hydration in the first step followed immediately by decomposition of the anions and ligand molecules in the subsequent steps.^[28, 29] Considering the TGA results in the work, some remarks and conclusions can be drawn as follows:

- (1) There are two kinds of H_2O molecules, *i.e.*, hydrated and coordinated
- (2) The thermal decomposition of complexes includes several steps

Mohamed and coworkers have reported the preparation of metal complexes of Schiff base (HL) (Fig. 17) ligand, prepared via condensation of 4-aminoantipyrine and 2-aminophenol. The thermal behavior of these chelates showed that the hydrated complexes lose H_2O , HCl , and $\text{C}_2\text{H}_8\text{O}$ molecules of hydration in the first two steps followed immediately by decomposition of the anions and ligand molecules in the subsequent steps. The activation thermodynamic parameters were calculated from the DTG curves by using the Coats–Redfern method.^[30]

A new series of metal complexes of Cd(II), Cu(II), Ni(II), and Co(III) with Schiff base ligand, H_2L , 2-(Hydroxybenzylidene) thiosemicarbazone were synthesized. The mixed ligand complexes were prepared by using glycine (Gly), 2-aminopyridine (2-Ampy), and 1.10-phenanthroline (Phen) as secondary ligands. The structure of these complexes was identified and confirmed by elemental analysis, molar conductivity, UV–Vis, FTIR, and ^1H NMR spectroscopy, and magnetic moment measurements as well as TGA–DSC technique. The discussions of the prepared complexes indicate that the ligand behaves as a monoanionic tridentate ligand through ONS donor sites. Thermal studies suggested a mechanism for the degradation of the metal complexes as a function of temperature supporting the chelation modes and showed the possibility of obtaining new complexes pyrolytically in the solid state which cannot be synthesized from the solution.^[31]

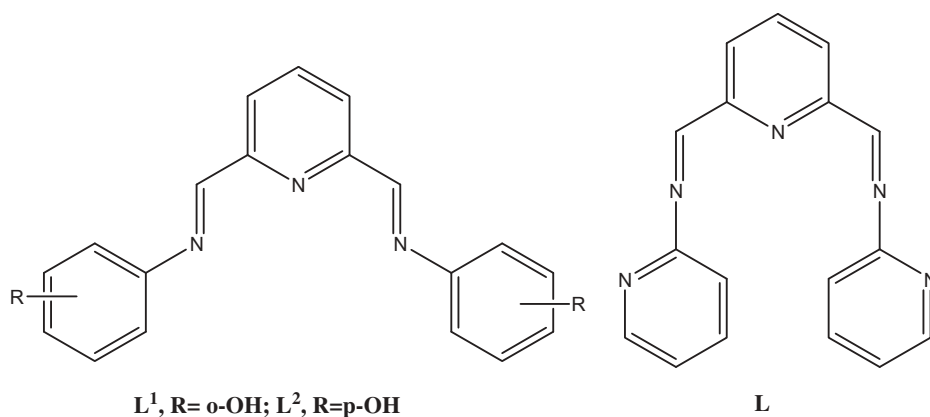


Figure 16. The structures of Schiff bases.

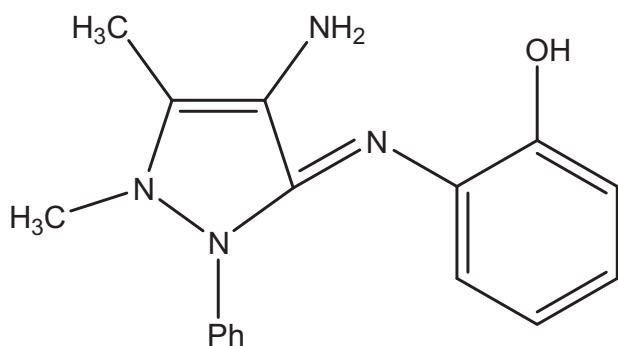


Figure 17. Structure of Schiff base (HL).

Royo et al.^[32] have reported the study of a series of complexes of the type $(C_6F_5)CoL_4B$ with tetradentate ligands acacen (N,N'-ethylene-bis acetylacetonimine diaion), mesalen (N,N'-ethylene-bis-7,7'-dimethylsali-cylideneimine dianion) and dotOH (diacetylmonoxi-meiminodacetyl-monoximateiminopropane-1,3-mono-anion), respectively using TGA and DTA methods to obtain information concerning the decomposition mechanism and the influence of the ligands on the thermal stabilities of cobalt-carbon and cobalt-axial base bond. The elimination of the axial base led to the formation of pentacoordination complexes $(C_6F_5)CoL_4$ (when $L_4 = \text{acaen, mesalen}$) and their subsequent decomposition involved cobalt-carbon rupture to form CoL_4 . In contrast, the latter reaction occurs first when the tetradentate ligand was dotnH. It has been observed that the stability of the cobalt-carbon bond was related to the nature of the equatorial ligands, and decreases in the following order: mesalen > acacen > dotnH.^[32] Taking into account the importance of thermal stability in the liquid crystal field, the study presents the thermal behavior of some ferrocene-containing Schiff bases. Some other kinetic characteristics, such as reaction order (n), activation energy (E_a),

and pre-exponential factor ($\ln A$) have been also evaluated.^[33]

In previous works, 4-(thiophen-3-yl)-aniline undergoes condensation with o-vanillin to form an ONS donor Schiff base, 2-methoxy-6-[(4-thiophene-3-yl-phenylimino)-methyl]-phenol, which forms complexes of the type $[ML_2] \cdot xH_2O$ (where $M = Mn, Co, Ni, Cu, Zn, Pd$). These complexes were characterized by elemental analysis, 1H NMR, electronic, mass, and IR spectroscopies and conductance measurements. The results indicated that the ligand (HL) decomposed in three steps. The first step involved the loss of the fragment, C_2H_2 and 0.5 mol N_2 at $30^\circ C - 220^\circ C$. The second step involved the loss of the organic fraction, $C_{11}H_8O_2S$ at $220^\circ C - 420^\circ C$. The final step was the loss of the fragment, C_5H_5 at $420^\circ C - 700^\circ C$.^[34]

Indirs and coworkers have reported the study of TGA, DTG, and DTA curves of CoL_2 and $Pd(LH)_2Cl_2$ ($LH = \text{salicylidene-2-aminofluorene}$ and $2\text{-hydroxy-1-naphthalidene-2-aminofluorene}$) in air. Mass loss considerations at main decomposition stages indicated conversion of the complex to oxides. The mathematical analysis of TGA data showed that the first-order kinetics was applicable in all cases. Kinetic parameters (energy and entropy of activation and preexponential factor) were reported in this study.^[35]

Schiff base metal complexes derived from 2-thiophene-carboxylidene-4-anisidine (TCA), 3,4-dihydroxy-5-nitrobenzylidene-2-amino-5-methylthiazole (DAT), and 3,4-dihydroxy-5-nitrobenzylidene-4-chloroaniline (DCA) (Fig. 18) have been synthesized and characterized by elemental analysis, IR, UV-Vis, molar conductance, and thermal analyses. These complexes were colored and stable in air at room temperature. The complexes exhibited coordination numbers to be 4 and 6. The thermal behavior of metal complexes shows that the hydrated complexes lose water molecules of hydration in the first and then is immediately followed by decomposition of ligand molecules in

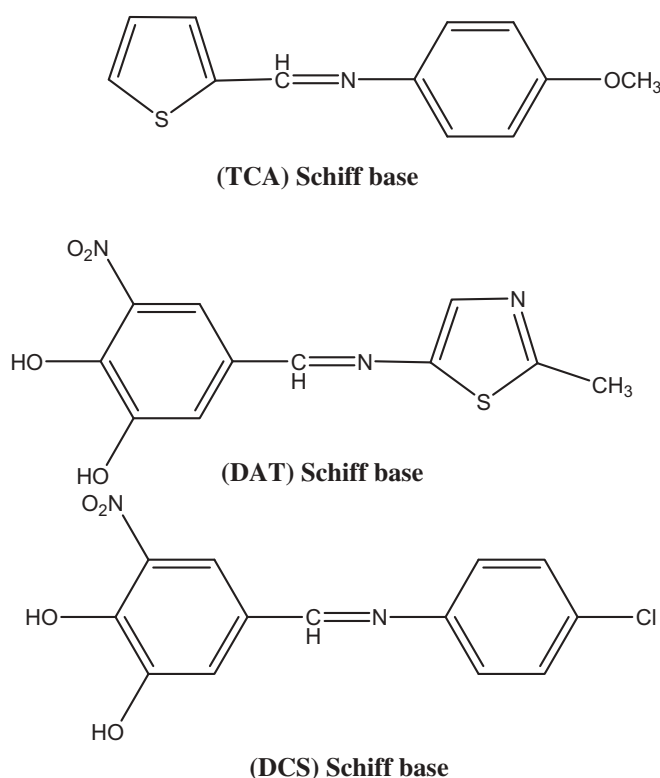


Figure 18. Suggested structure of Schiff base ligands.

the subsequent steps. Moreover, thermal data showed degradation pattern of the complexes. TGA, DTA, and DTG studies also guide to thermodynamic, kinetic, and reactivity behavior of materials and metal-ligand interaction.^[36]

Ghammamy et al.^[37] synthesized and characterized N,N'-bis (2-hydroxy- α -methyl benzylidene) isobutyl daimine (Fig. 19). In this research, some of the inorganic complexes of uranyl with N-donor ligands were synthesized. Complexes were characterized by FTIR, UV-Vis, ¹H NMR, ¹³C NMR spectra, TGA/DTG measurements, and some physical properties. The results of the simultaneous TGA-DTG-DTA of the complexes showed that the final degradation product for these complexes is UO₃.^[37]

Khalaji et al.^[38] have reported the synthesis nanoparticles of Co₃O₄ by solid-state thermal decomposition of the Co(II) macrocyclic Schiff base complexes [CoL1] (1) and [CoL2] (2)(Fig. 20) as precursor at 450°C for 3 hrs without employing toxic solvent or surfactant and complicated equipment. The products were characterized by FTIR, UV-Vis spectroscopy, XRD, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The results showed that the Co₃O₄ products are pure and single phase. The optical spectra of the Co₃O₄ products indicated two direct band gaps at about 1.4 and 2.5 eV.^[38]

Asadi et al. have reported the synthesis and characterization of some tetradentate salen-type Schiff bases and their uranyl complexes by UV-Vis, NMR, IR, TGA, C.H. N., and X-ray crystallographic studies. In addition, the kinetic parameters of complexes were calculated from thermal analysis. The thermal decomposition reactions were first order for the studied complexes.^[39, 40]

Metal complexes of niobium (V) with 3-substituted-4-amino-5-mercapto-1,2,4-triazole Schiff (Fig. 21) bases have been synthesized in dry chloroform under a nitrogen atmosphere. Parameters, such as energy of activation (E_a), enthalpy (ΔH^\ddagger), entropy (ΔS^\ddagger), and Gibbs energy (ΔG^\ddagger), were computed from the thermal decomposition data. Based on the spectral and thermal studies, a coordination number of seven is proposed.^[41]

Khalil and coworkers have reported the preparation of a novel, simple approach to the synthesis macrocyclic Schiff base ligand resulted from the condensation of bisaldehyde and ethylenediamine (7, 8, 15, 16, 17, 18-hexahydrodibenzo (a, g) (14) annulene)(L) and its complexes using different physicochemical studies as elemental analysis, FTIR, ¹H NMR, conductivity, magnetic properties, thermal analysis, and their biological activities.^[42]

Karuna et al. have reported the synthesis of three series of Schiff bases, namely 2-(4-alkoxy-2-hydroxybenzylideneamino) fluorenes(1), 4-(4-alkoxy-2-

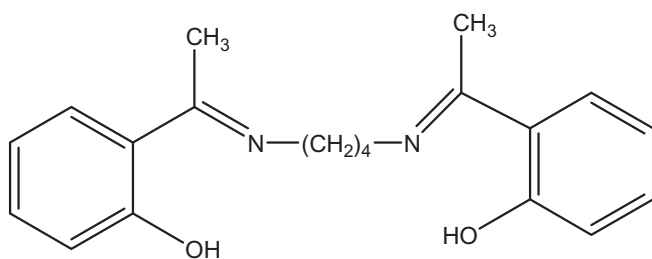


Figure 19. Chemical structure of HMBUD.

hydroxybenzylideneamino)biphenyls (2), and 4-(4-alkoxy-2-hydroxybenzylideneamino)stilbenes(3), respectively. The thermal behavior of all the ligands and the complexes was investigated by using polarizing microscopy and differential scanning calorimetry.^[43]

In order to develop new metallo-antimicrobials, the complexes of type $MLCl \cdot nH_2O$ ((1) M: Co, $n = 0$; (2) M: Ni, $n = 2$; (3) M: Cu, $n = 2.5$; (4) M: Zn, $n = 0$, HL: Schiff base derived from acetylacetone and 3-amino-4H-1.2.4-triazole) were synthesized by template condensation. Processes as water elimination, melting, chloride anion removal, as well as oxidative degradation of the complexes were observed. The temperature ranges as well as modification in the electronic spectra of dehydrated intermediates indicate the presence of both coordination and crystallization water molecules. Moreover, thermal decomposition of complexes allowed establishing the number and nature of water molecule, the composition of complexes, and the intervals of thermal stability. The water elimination in one or two well-defined events was observed for hydrated complexes. Schiff bases complexes undergo hydrochloric acid elimination, evidenced as endothermic process on DTA curve, process that in some cases was overlapped with partial oxidative degradation of Schiff base. Finally, the organic ligand decomposes in one or two

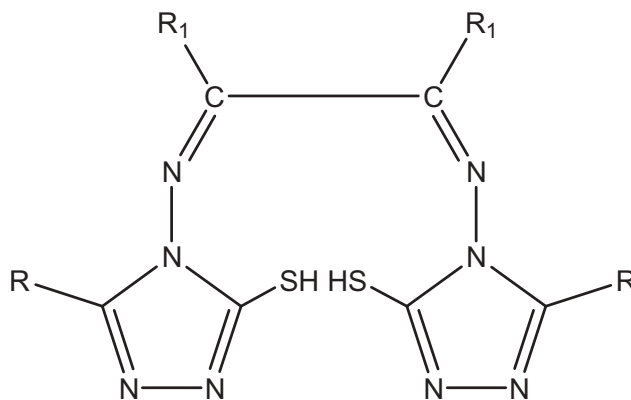


Figure 21. Structure of ligand.

steps, leading to metal oxide as residue. The anhydrous complexes melt before the thermal decomposition starts, behavior that indicates a high degree of covalency for these species that adopt a tetrahedral stereochemistry.^[44]

Cationic iron (III) complexes of the type $[FeLn(H_2O)_2]NO_3$ ($n = 1$ or 2) were accessed from the interaction of $Fe(NO_3)_3 \cdot 9H_2O$ with $[N_2O_2]$ donor Schiff base (L) in 1:1 molar ratio. The Schiff base ligands (Fig. 22) were prepared from condensation of 2-hydroxy-1-naphthaldehyde with *o*-phenylenediamine or ethylenediamine in 2:1 molar ratio. The thermal study provided unambiguous evidence for the occurrence of coordinated water in the complexes. In addition, the TGA-DTA data were consistent with the proposed structures and provided unambiguous evidence for coordinated water in the complexes.^[45]

Cavalherio et al.^[46] have reported the preparation and characterization of the Schiff base complexes by UV, IR, and NMR (1H and ^{13}C) spectroscopy, elemental analysis, and XRD. Free ligand and some new complexes were submitted to thermal analysis (TGA

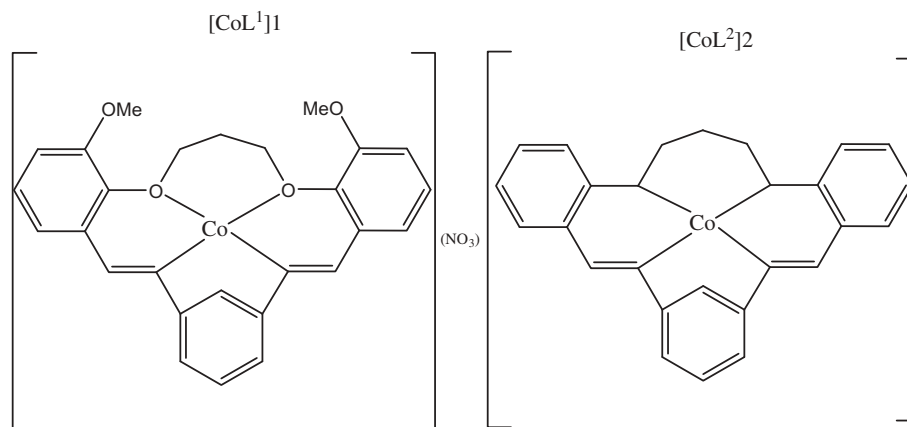


Figure 20. The Chemical structure of $[CoL^1](1)$ and $[CoL^2](2)$.

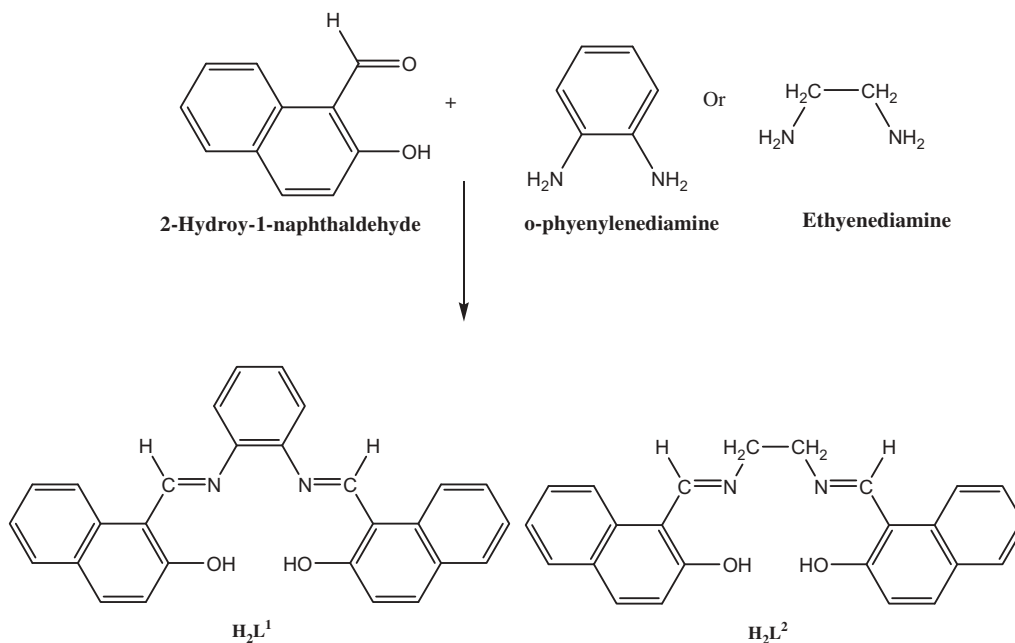


Figure 22. Synthesis of Schiff base ligands.

and DSC) under dynamic air atmosphere. The differences in the decomposition profiles were related to the structure of isomers and decomposition intermediate were characterized according to their XRD.

Alex and coworkers have reported the synthesis of a bidentate Schiff base ligand namely, N,N'-1.3-benzodioxol-5-ylmethylene] butane-1.4-diamine by condensing piperonal (3.4-dioxymethylenebenzaldehyde) with butane-1.4-diamine. Cr(III), Mn(II), and Fe(III) complexes of the chelating ligand were synthesized using acetates, chloride, bromide, nitrates, and perchlorates of these metals. The thermograms of three complexes were analyzed and the kinetic parameters for the different stages of decomposition were determined. Based on temperature and activation energy, for the decomposition of complexes, stabilities of the complexes were found to be in the order, Cr>Mn>Fe^[47, 48]

Cobalt(II) complexes of a new series of unsymmetrical Schiff bases have been synthesized and characterized by their elemental analyses, melting points, magnetic susceptibility, TGA, DSC, IR, and electronic spectral measurements. The purity of the ligands and the metal complexes were confirmed by microanalysis, while the unsymmetrical nature of the ligands was further corroborated by ¹H NMR. A comparison of the IR spectra of the Schiff bases and their metal complexes shows that the Schiff bases are tetradentate and coordinated via N₂O₂ chromosphere. The complexes were thermally stable up to 372.3°C and their thermal decomposition was generally through the partial loss of the organic moiety.^[49]

Angela and coworkers have reported the preparation of new copper (II) complexes of Schiff bases with 1,2-di(imino-2-aminomethylpyridil)ethane with the general composition CuLX_m(H₂O)_x, [L = Schiff base, X = Cl⁻, Br⁻, NO₃⁻, ClO₄⁻, CH₃COO⁻, m = 2; X = SO₄²⁻, m = 1] by template synthesis. The thermal behavior of complexes was studied using TGA, DTA, and DSC.^[49]

Some new Schiff base metal complexes of Cr(III), Co(II), Ni(II), and Cu(II) derived from N-(4-chlorobenzylidene)-5-methyl-1,3-thiazol-2-amine (CBAM) and N-[4-(dimethylamino) benzylidene]-6-nitro-1,3-benzothiazol-2-amine (DBAT) have been synthesized by conventional as well as microwave methods. These compounds have been characterized by elemental analysis, FTIR, FAB-mass, molar conductance, electronic spectra, ESR, magnetic susceptibility, thermal, electrical conductivity, and XRD analysis. The thermal behavior of metal complexes shows that the hydrated complexes firstly lose molecules of hydration followed by decomposition of ligand molecules in the subsequent steps.^[50]

A series of new homo-binuclear nano Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) complexes were prepared using a Schiff base ligand based on p-phenylenediamine and 2-hydroxy-1-naphthaldehyde. The prepared complexes were characterized using elemental, thermal analyses, FTIR, ¹H NMR, ¹³C NMR, UV-Vis, XRD, SEM, molar conductance, and magnetic moment measurements. The geometries proposed are mainly octahedral configuration which surrounds the central atoms referring to the electronic spectral data and magnetic measurements. The calculations abstracted from XRD patterns

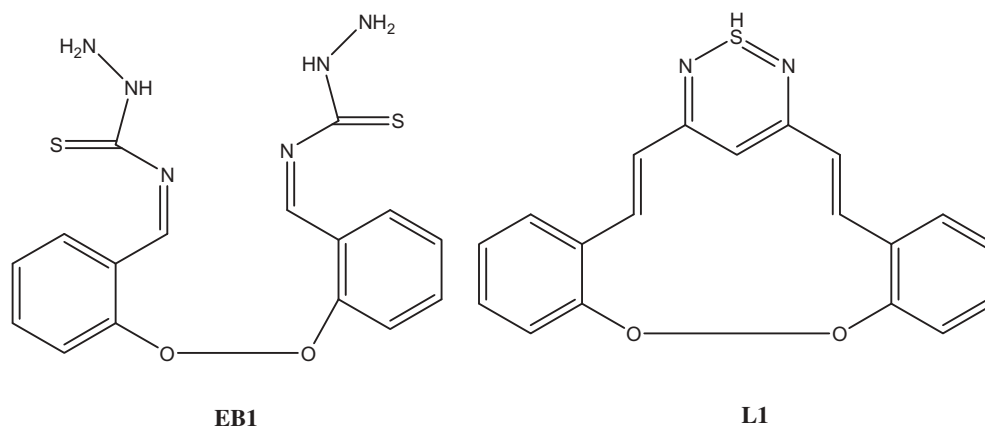


Figure 23. Preparation of EB1 and L1 Schiff's bases.

propose the nano-sized complexes. In this work, TGA was used to ensure the nature of the presence of solvent molecules attaching to the complexes. Molecular modeling was carried out to assert the structural formula proposed for the ligand and some of its Schiff base complexes.^[51]

Sohan et al. have reported the synthesization of the Schiff bases of chitosan by the reaction of chitosan with different aromatic aldehydes. The prepared ligands are characterized by FTIR, ¹H NMR spectroscopy, and elemental analysis (C, H, N). In addition, TGA of Schiff base polymers shows that they have nearly the same decomposition temperature as the chitosan, indicating that Schiff bases are thermally stable.^[52]

Dorovskikh et al. have obtained the ligands with Schiff bases in the condensation of propylenediamine or 2,2-dimethylpropylenediamine with acetylacetonone (Hacac) in the 1:2 molar ratio. The Schiff bases are analyzed by the elemental analysis methods, $T_{\text{melt}} = 90^{\circ}\text{C}$ – 92°C for pda(acac)₂ (N,N'-propylene-bis(acetylacetoniminato)), $T_{\text{melt}} = 84^{\circ}\text{C}$ – 86°C for dmpda(Hacac)₂ (N,N'-2,2-dimethylpropylene-bis(acetylacetoniminato)). The tautomerism of the ligands is established by the single-crystal XRD analysis, IR spectroscopy, ¹H NMR spectroscopy, and ¹³C NMR spectrometry. The synthesized complexes [Cu(pda(acac)₂)] (1), $T_{\text{melt}} = 121^{\circ}\text{C}$ – 122°C and [Cu(dmpda(acac)₂)] (2), and $T_{\text{melt}} = 156^{\circ}\text{C}$ – 158°C are studied by the XRD method.^[53,54] Therefore, two pyridine carboxaldehyde-derived Schiff bases and their copper, nickel, and manganese complexes have been synthesized and characterized by spectroscopic and thermal analyses.^[55]

In the recent works, two Schiff's bases (Fig. 23) as new macrocyclic compounds were prepared via condensation reactions between bisaldehyde (2,20-(ethane-1,2-diylbis(oxy))dibenzaldehyde): firstly with hydrazine carbothioamide and secondly with 4,6-diaminopyrimidine-2-thiol. The structures of these compounds obtained were

characterized based on elemental analysis, FTIR, and ¹H NMR spectra, mass (MS), and thermal analyses (TA). The results indicated that the less negative entropy values may refer to increase of disorder during the decomposition of this Schiff base, which may be attributed to the less stability of this Schiff base. The negative value of entropy may refer to the chemical rearrangement and/or chemical recombination of the L1 fragments.^[56]

Belal et al.^[57] have reported the preparation of three Schiff's bases, namely (Fig. 24) (2(1-hydrazonoethyl)phenol), (2, 4-dibromo 6-(hydrazonomethyl)phenol), and (2 (hydrazonomethyl)phenol) as new hydrazone compounds via condensation reactions with molar ratio (1:1) of reactants. The structures of these compounds were characterized by elemental analysis (EA), mass (MS), FTIR and ¹H NMR spectra, and thermal analyses (TGA, DTG, and DTA). The activation thermodynamic parameters, such as ΔE , ΔH , ΔS , and ΔG were calculated from the thermogravimetric curves using the Coats–Redfern method. Consequently in the present work, the obtained thermal (TA) and mass (MS) practical results were confirmed by semi-empirical MO-calculations (MOCS) using the PM3 procedure.^[57]

Conclusions

In this work, some conclusions can be drawn as follows:

- (1) There were two kinds of H₂O molecules, *i.e.*, hydrated and coordinated in Schiff base complexes.
- (2) The thermal decomposition of complexes includes several steps.
- (3) The thermal behavior of metal complexes shows that the hydrated complexes firstly lose water molecules of hydration followed by

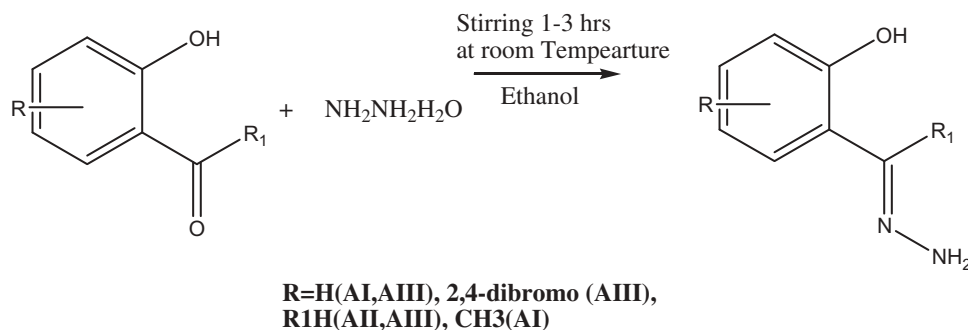


Figure 24. Preparation of Schiff's bases.

- decomposition of ligand molecules in the subsequent step.
- (4) Thermal data showed degradation pattern of the complexes. TGA, DTA, and DTG studies also guide to thermodynamic, kinetic, and reactivity behavior of materials and metal–ligand interaction.
 - (5) The thermal decomposition reactions were first order for the studied complexes.
 - (6) The thermal decomposition pathways of the complexes were related to the Schiff base properties.

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