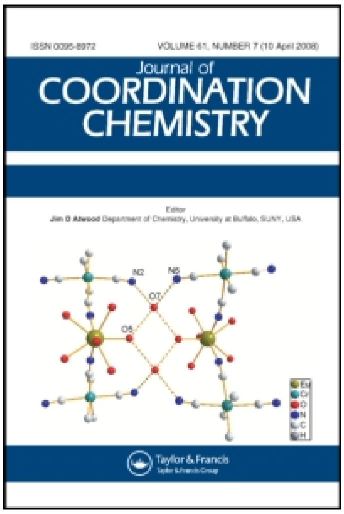

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Microwave assisted synthesis and characterization of N,N'-*bis*(salicylaldehydo)ethylenediimine complexes of Mn(II), Co(II), Ni(II), and Zn(II)

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Microwave assisted synthesis and characterization of N,N′-*bis*(salicylaldehydo)ethylenediimine complexes of Mn(II), Co(II), Ni(II), and Zn(II)

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Microwave chemistry is a green chemical method that improves reaction conditions and product yields while reducing solvent amounts and reaction times. The main aim of this article is to synthesize the tetradentate N_2O_2 ligand [HO(Ar)CH=N–$(CH_2)_2$–N=CH(Ar)OH] and manganese(II), cobalt(II), nickel(II), and zinc(II) complexes of the type ML by classical and microwave techniques. The resulting Schiff base and its complexes are characterized by ^{1}H NMR, infrared, elemental analysis, and electronic spectral data. The ligand and its Co(II) and Mn(II) complexes were further identified by X-ray diffraction and mass spectra to confirm the structure. The results suggest that the metal is bonded to the ligand through the phenolic oxygen and the imino nitrogen.

Keywords: Microwave assisted synthesis; Synthesis of Schiff base; Metal ligand complex

1. Introduction

Schiff bases containing an azomethine group (–CH=N–) are formed by condensation of a primary amine with a carbonyl compound [1]. These bases are ligands which are active, well designed, and stable under a variety of oxidative and reductive conditions [2]. Symmetric and asymmetric transition metal complexes of Schiff bases have been used as catalysts in reactions, such as epoxidation [3], asymmetric synthesis [4], asymmetric sulfoxidation [5], asymmetric silylcyanation [6], and many other applications [7]. Schiff bases and the relevant transition metal complexes are widely studied because they have industrial, antifungal, antibacterial, anticancer, and herbicidal applications [8]. These complexes play an important role in the development of coordination chemistry [9] and possess important properties, such as biological activity [10], catalytic activity [11], and photochromic properties [12].

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Schiff bases continue to occupy an important position as ligands in metal coordination chemistry almost a century since their discovery.

Schiff bases derived from the reaction of salicylaldehyde with primary amines (salen type Schiff base) represent a versatile series of ligands and much have been well known in the field of organometallics [13]. Transition metal complexes of this ligand, as catalysts, have attracted significant attention for their applications, particularly in agrochemical and pharmaceutical industries. Recent use of these complexes as catalytically active materials to develop surface-modified electrodes for sensor applications has stimulated the use of cyclic voltammetry as a technique to study structure–reactivity relationships for this class of compounds [14–16].

Ribeiro da Silva *et al*. [17] reported molecular thermochemical study of salen and its Ni(II), Cu(II), and Zn(II) complexes and the thermochemical properties of N_2O_2 Schiff-base ligands. Canpolat *et al*. [18] reported the synthesis and characterization of a new 5-bromosalicylidene-p-aminoacetophenoneoxime and its complexes with Co(II), Ni(II), Cu(II), and Zn(II). Nair and Lal *et al*. [19] reported synthesis and spectroscopic studies of complexes of Cu, Ni, Fe, and Zn. Laskin *et al*. [20] reported gas-phase fragmentation of ternary complexes of angiotensin analogues with trivalent metal-salen peptide complexes. Kulkarni *et al*. [21] reported synthesis, DNA cleavage and antimicrobial studies of La(III), Th(IV), and VO(IV) complexes with Schiff bases derived from coumarin and o-phenylenediamine/ethylenediamine. Kaczmarek *et al*. [22] have carried out the self-assembled synthesis, characterization, and antimicrobial activity of zinc(II) N,N′-*bis*(salicylidene)-4-methyl-1,3-phenylenediamine (H_2L) complexes. Kwong *et al*. [23] reported reaction of a (salen) ruthenium(VI) nitrido complex with isocyanide. Xu *et al*. [24] reported the X-ray crystal structures of *cis*-*β*-*bis*(carbonyl) ruthenium-salen complexes and catalytic properties toward asymmetric intramolecular cyclopropanation. Rao *et al*. [25] employed the ESI method in combination with MS/MS to study the binding of 4-(N,N-dimethylamino)pyridine to salen- and salanCr(III) complexes and characterized by collision-induced dissociation (CID) and catalytic activity for CO_2/epoxide copolymerization.

Microwave assisted reactions in solvent or solvent-free conditions have gained popularity because of rapid reaction rate, cleaner reactions, ease of manipulation, higher yields, and often, improved selectivity, with respect to conventional reaction conditions [26]. A major advantage is given by the usual reaction time which is a few minutes even on a few hundred grams scale. The reduction of solvents and formation of lowered amounts of by-products decrease pollution at the source and ensure high levels of "atom economy". Another advantage of microwave-induced organic reaction enhancement (MORE) chemistry techniques is lowered energy consumption compared to conventional reactions performed under reflux which also require the latent heat of vaporization. The present study investigates reaction of tetradentate Schiff base synthesized by classical and microwave technology, by condensation of ortho-hydroxybenzaldehyde and 1,2-diaminoethane for synthesis of N,N′-*bis*(salicylaldehydo)ethylenediimine and its complexes with manganese, cobalt, nickel, copper, and zinc ions. The prepared ligand and metal complexes were characterized by ^1H NMR, infrared, elemental analysis, and electronic spectral data. The ligand and its Co(II) and Mn(II) complexes were further identified using X-ray diffraction (XRD) and mass spectra.

2. Experimental

2.1. *General*

All chemicals and solvents used for synthesis were of analytical reagent grade. Manganese(II), cobalt(II), nickel(II), and zinc(II) acetates from Merck were used without purification.

2.2. *Physical measurements*

Microwave assisted condensation of Schiff base and complexes were carried out in a domestic oven, 2450 MHz frequency, 800W. IR spectra were recorded on a Shimadzu Dr-8031 instrument. Electronic spectra from 200 to 800 nm were determined in DMSO on a Cintra 10e spectrometer. The ^{1}H NMR spectra of the Schiff base and metal complexes were recorded on a Bruker-Avance (300 MHz), Varian-Gemini (200 MHz) spectrophotometer using DMSO and TMS as the internal standard. ESI-MS spectra were determined on a LCQ ion trap mass spectrometer (Thermo Fisher, San Jose, CA, USA), equipped with an ESI source. Elemental analyses were carried out using a Perkin-Elmer CHNS/O elemental analyzer model 2400. The XRD patterns for all the samples are obtained on a Rigaku miniflex X-ray diffractometer using Ni filtered Cu-Kα radiation ($\lambda = 1.5406$) from $2\theta = 2$–80°, at a scan rate of $2^\circ \mathrm{min}^{-1}$, with the beam voltage and a beam current of 30 kV and 15 mA, respectively.

2.3. *Synthesis of Schiff base (H_2L)*

2.3.1. Microwave method. A mixture of (0.0081 mol) ortho-hydroxybenzaldehyde, (0.004 mol) 1,2-diaminoethane and ethanol were placed in a flask and irradiated in a microwave oven for 20 s. Completion of the reaction was monitored by TLC. The reaction mixture was allowed to attain room temperature, the solid washed with aq. ethanol and recrystallized from methanol. Yellow crystals; UV-Vis (λ_{max} in nm): 322, 268; XRD, *d* values: 15.02, 7.55, 5.04, 4.68, 4.43, 4.16, 3.78, 3.09, 3.03, 2.16, and 2.10; IR (KBr, cm^{-1}): 1636 (–C=N–); ^{1}H NMR (300 MHz, DMSO) δ (ppm) = 3.9 (s, 4H, CH_2–CH_2); 8.4 (s, 2H, –CH=N–); 6.8–7.3 (m, 8H, Arom-H); 12.9 (s, 2H, –OH); mass spectra, $m/z = 268$ (100%).

2.3.2. Classical method. Ortho-hydroxybenzaldehyde (0.016 mol), 0.0081 mol of 1,2-diaminoethane, and 20 mL of ethanol were refluxed for 20 min. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled and crystallization was induced by rubbing with a glass rod. The solid was collected by filtration and washed well with aq. ethanol. The crude product was recrystallized from methanol. Spectral data were similar to those reported by the microwave method.

2.4. *Synthesis of metal complexes*

2.4.1. Microwave method. Schiff base (0.003 mol) was added to a ethanolic solution of $M(CH_3COO)_2 \cdot 4H_2O$ (M = Mn, Co, Ni, Cu, and Zn). The resulting mixture was irradiated in a microwave oven for 1 min. The solid complex precipitated was filtered, washed thoroughly with hot ethanol, and dried in an oven.

2.4.2. Classical method. A solution of metal(II) acetate in ethanol (0.003 mol) was refluxed with an ethanolic solution of the Schiff base (0.003 mol) for ~5 h. The solution was then reduced to one-third on a water bath. The solid complex precipitated was filtered, washed thoroughly with hot ethanol, and dried in an oven. Spectral data were similar to those reported in section 2.4.1.

2.4.3. Metal complex (Mn). Dark green crystals; UV-Vis (λ_{max} in nm): 365, 260; XRD, *d* values: 8.33, 7.96, 7.14, 6.31, 6.02, 5.72, 5.05, 4.90, 4.77, 4.51, 4.40, and 4.21; IR (KBr, cm^{-1}): 1600 (–C=N), 510 (Mn–N), 414 (Mn–O); ^1H NMR (300 MHz, DMSO) δ (ppm) = 3.9 (s, 4H, CH_2–CH_2); 8.2 (s, 2H, –CH=N–); 6.5–7.3 (m, 8H, Arom-H).

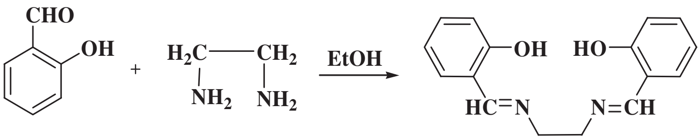
2.4.4. Metal complex (Co). Dark brown crystals; UV-Vis (λ_{max} in nm): 402, 264; XRD, *d* values: 13.33, 12.48, 9.06, 8.47, 7.56, 6.31, 6.13, 4.58, 4.38, 4.20, and 3.57; IR (KBr, cm^{-1}): 1603 (–C=N–), 540 (Co–N), 443 (Co–O); ^1H NMR (300 MHz, DMSO) δ (ppm) = 3.8 (s, 4H, CH_2–CH_2); 8.0 (s, 2H, –CH=N–); 6.8–7.2 (m, 8H, Arom-H); mass spectra, $m/z = 325$ (100%).

2.4.5. Metal complex (Ni). Red solid; UV-Vis (λ_{max} in nm): 410, 262; IR (KBr, cm^{-1}): 1624 (–C=N–), 520 (Ni–N), 430 (Ni–O); ^1H NMR (300 MHz, DMSO) δ (ppm) = 3.8 (s, 4H, CH_2–CH_2); 8.2 (s, 2H, –CH=N–); 6.6–7.2 (m, 8H, Arom-H).

2.4.6. Metal complex (Zn). Yellow solid; UV-Vis (λ_{max} in nm): 366, 261; IR (KBr, cm^{-1}): 1633 (–C=N–), 532 (Zn–N), 415 (Zn–O); ^1H NMR (300 MHz, DMSO) δ (ppm) = 3.7 (s, 4H, CH_2–CH_2); 8.3 (s, 2H, –CH=N–); 6.4–7.1 (m, 8H, Arom-H).

3. Results and discussion

The Schiff base forms complexes with metal ions via N and O donors; phenolate oxygen is a hard donor which stabilizes higher oxidation states while imine nitrogen is a softer donor, stabilizes lower oxidation states of metals [27]. Preparation of the ligand is represented in scheme 1. Reaction of Mn-, Co-, Ni-, and Zn acetate with tetradentate Schiff-base ligand (H_2L) in 1 : 1 molar ratio in ethanol is represented in scheme 2. The microwave assisted (MWI) synthesis of Mn-, Co-, Ni-, and Zn acetate with tetradentate Schiff base (H_2L) in 1 : 1 molar ratio in ethanol is represented in scheme 3. It is clear from the yield comparison plot (figure 1) of classical and MWI synthesis of the Schiff



Scheme 1. Preparation of H_2L: classical method = 20 min, 76%; microwave method = 20 s, 88%.

$$M(CH_3COO)_2 + H_2L \xrightarrow[\text{5 h}]{\text{EtOH, heat}} ML + 2CH_3COOH$$

Scheme 2. Reaction of M=Mn-, Co-, Ni-, and Zn acetate with tetradentate Schiff base.

$$M(CH_3COO)_2 + H_2L \xrightarrow[\text{1min}]{\text{EtOH, MW}} ML + 2CH_3COOH$$

Scheme 3. Microwave irradiation of metal acetates with tetradentate ligand.

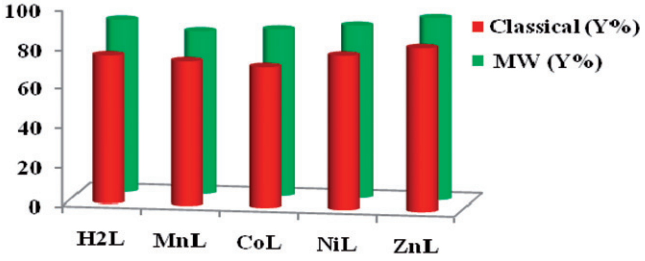


Figure 1. Graphical representation of yield comparison between classical and microwave irradiations.

base and its metal complexes that MWI is easier, convenient, and the yield of all products are better than the classical method.

The complexes are air-stable, non-hygroscopic, colored solids, insoluble in water, partly soluble in ethanol and methanol, and soluble in DMSO and DMF. The Schiff base and its Mn(II) and Co(II) complexes were identified by X-ray powder diffraction pattern. X-ray powder diffraction peaks of Schiff base (H_2L) (Supplementary material) and its CoL and MnL complexes have been indexed by the crystal system. The observed interplanar spacing values (‘*d*’ in Å) have been measured from the diffractograms. Elemental analysis data of the Schiff base and metal complexes (table 1) are consistent with the calculated results from the empirical formula of each compound.

In the microwave method, the yield of Schiff base and its transition metal complexes are better than the classical method. Microwave irradiation facilitates polarization of the reacting molecule causing fast reaction to occur. A comparative study of yield and reaction time is shown in table 2. Compared to thermal heating, microwave heating has many benefits, such as rapid volumetric heating, higher reaction rates, higher reaction selectivity, higher product yield, and energy saving [28]. In microwave heating, energy

Table 1. Elemental analysis and electronic spectral data of the complexes.

	% Calcd (Found)				Wavelength (nm) in DMSO
	C	H	N	M	
H_2L	71.62 (71.41)	5.01 (5.08)	10.44 (10.35)		322, 268
MnL	59.80 (59.32)	4.36 (3.28)	8.72 (8.60)	17.13 (17.21)	365, 260
CoL	59.07 (59.01)	4.30 (4.21)	8.61 (8.52)	18.15 (18.38)	402, 264
NiL	59.13 (59.26)	4.31 (4.35)	8.62 (8.56)	18.07 (18.16)	455, 410, 262
ZnL	57.94 (57.98)	4.22 (4.49)	8.45 (8.40)	19.73 (19.75)	366, 261

Table 2. Physical properties of the Schiff base and its metal complexes.

				Microwave method		Classical method	
Compound	Ligand/Complex	Color	Formula weight	Reaction time (s)	Yield (%)	Reaction time (h)	Yield (%)[a]
H_2L	$C_{16}H_{16}N_2O_2$	Yellow (crystals)	268	20	88	0.33	76
MnL	$C_{16}H_{14}N_2O_2Mn$	Dark green (crystals)	321	60	83	5	74
CoL	$C_{16}H_{14}N_2O_2Co$	Dark brown (crystals)	325	60	85	5	72
NiL	$C_{16}H_{14}N_2O_2Ni$	Red	324	60	88	5	79
ZnL	$C_{16}H_{14}N_2O_2Zn$	Yellow	330	60	93	5	84

[a] Isolated yields.

source of the microwaves is not in direct contact with the reaction solution, so the heat produced is via dielectric heating, which leads to completely different temperature profiles [29].

3.1. *UV-Vis spectral studies*

Electronic spectral data of the Schiff base and its complexes are summarized in table 1. The spectra of H_2L display two main peaks at 262 and 322 nm, the first peak attributed to benzene π–π^* and the second to n–π^* transition. The n–π^* transition was shifted to shorter wavelength with an increase in intensity. This shift is attributed to donation of the lone pairs of nitrogen of the Schiff-base ligand (H_2L) to the metal ion ($N \rightarrow M$) [30]. The Mn(II) complex is dark green in solution and shows an intense absorption in the visible region at 365 nm assigned to ${}^6A_1 \rightarrow {}^4T_1$ transition, suggesting a tetrahedral geometry for the Mn(II) complex. The electronic spectrum of the dark brown Co(II) complex exhibits a band at 402 nm assigned to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ for square-planar geometry. Square-planar Ni(II) complexes are commonly orange or red; Ni(II) complex shows absorption in the visible region at 455 nm with a second band at 410 nm. These bands are commonly assigned to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$), respectively. The electronic spectra of Zn(II) complex exhibits intensity at 366 nm due to ligand–metal charge transfer. These values are comparable to those of other reported complexes [31–36].

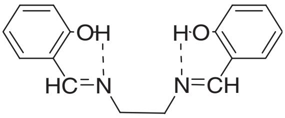


Figure 2. Structural representation of the hydrogen bonding.

3.2. ^{1}H NMR spectral studies

The ^{1}H NMR spectrum of the Schiff base shows the following signals: CH_2–CH_2 at 3.9 ppm (s, 4H), –CH=N– at 8.4 ppm (s, 2H), Arom-H at 6.8–7.3 ppm (m, 8H), and –OH at 12.9 ppm (s, 2H). The ^{1}H NMR spectrum of the metal complexes shows absence of phenolic –OH, confirming involvement of the –OH proton in complexation. The azomethine proton in the spectrum of the metal complexes shows less intensity and shifts downfield compared to the free ligand, suggesting deshielding of the azomethine group due to coordination with metal. There is no appreciable change in other signals of these metal complexes.

3.3. IR spectra

IR spectra provide valuable information regarding the functional group attached to the metal. A strong band for H_2L at about 1280 cm^{-1} has no corresponding bands in the metal chelates and is assigned to hydrogen-bonded O–H in-plane bending (figure 2). This assignment is supported by the disappearance of the band when the hydroxy hydrogen is replaced by a metal. The spectra of the ligand exhibit broad medium intensity bands in the 2800–2900 cm^{-1} range assigned to intramolecular hydrogen bonding vibration (O–H $\cdots$ N). In spectra of complexes these bands disappear. The phenolic C–O stretching vibrations appeared at 1286 cm^{-1} in the Schiff base [37], but in the complexes shifted to lower frequency. Vibrations of the azomethine of the free ligands are observed at 1600–1640 cm^{-1}. In the complexes, these bands are shifted to lower frequencies, indicating that the nitrogen of azomethine is coordinated to the metal. New bands in the region 410–550 cm^{-1}, which were absent in the free ligand, can be attributed to metal–oxygen and metal–nitrogen bonds, respectively.

Thus, IR spectra give clear evidence that bonding of the ligand to the metal occurs through nitrogen and oxygen and that the ligands are tetradentate.

4. Conclusions

Microwave irradiation is becoming an increasingly popular method of heating, which replaces classical heating because it proves to be a clean, cheap, and convenient method. Often, it affords higher yields and results in shorter reaction times. In this article we reported the characterization of classical as well as microwave assisted synthesis of a tetradentate Schiff base and its complexation with Mn(II), Co(II), Ni(II), and Zn(II). In microwave synthesis the yield of all the products are more than 80%. The reaction

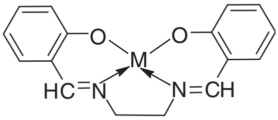


Figure 3. Structural representation of the Schiff-base complexes M = Mn, Co, Ni, and Zn.

time is drastically reduced to 1 min instead of 5 h in the classical preparation. Spectra reveal that transition metal is bonded to Schiff base through phenolic oxygen and imino nitrogen (figure 3).

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