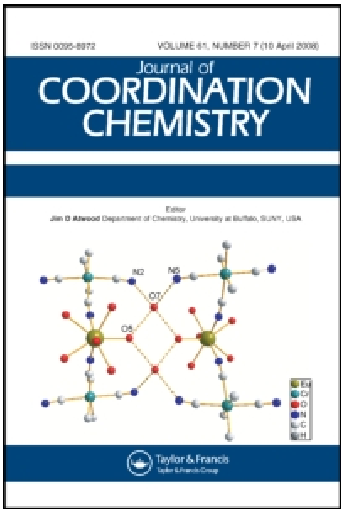

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Exploring microwave synthesis for co-ordination: synthesis, spectral characterization and comparative study of transition metal complexes with binuclear core derived from 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one

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To cite this Article Ali, Parvez , Ramakanth, P. and Meshram, Jyotsna(2010) 'Exploring microwave synthesis for co-ordination: synthesis, spectral characterization and comparative study of transition metal complexes with binuclear core derived from 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one', Journal of Coordination Chemistry, 63: 2, 323 — 329, First published on: 05 October 2009 (iFirst)

To link to this Article: DOI: 10.1080/00958970903305437

URL: http://dx.doi.org/10.1080/00958970903305437

Journal of Coordination Chemistry
Vol. 63, No. 2, 20 January 2010, 323–329

Exploring microwave synthesis for co-ordination: synthesis, spectral characterization and comparative study of transition metal complexes with binuclear core derived from 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one

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(*Received 16 April 2009; in final form 16 July 2009*)

A series of transition metal complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Hg(II), and Sn(II) has been synthesized from the Schiff base (L) derived from 4-aminoantipyrine and 4-fluoro-benzaldehyde using traditional synthetic methodology and microwave-induced organic reaction enhancement (MORE) technique. A benign, simple, and versatile route to a Schiff-base ligand and its metal complexes has been explored. Neat reactants were subjected to microwave irradiation giving the required products more quickly and in better yield compared to the classical methodology. Structural features were obtained from elemental analysis, molar conductivity, ^{1}H-NMR, mass, UV-Vis, and FTIR spectroscopy and X-ray diffraction. The data show that these complexes are ML_2. The MORE method for synthesis is easy, convenient, and ecofriendly as compared to the traditional synthetic method.

Keywords: Ligand; Complexes; MORE; Characterization

1. Introduction

Microwave irradiation on homogenous reaction mixtures and solid surfaces has emerged as a useful methodology for achieving better yields of product, significant reduction in reaction time, and reduction or elimination of environmentally detrimental solvents. For these reasons, microwave-assisted synthesis has become a rapidly growing field of study especially for various organic transformations [1]. Acceleration of reactions under microwave radiation can result from material–wave interactions leading to thermal effects [2, 3] or nonthermal effects [2]. The salient features of these high-yield protocols deal with enhanced reaction rates and ease of manipulation [4], advantageous for environmental reasons [5].

Schiff bases containing an azomethine group (–CH=N–) are formed by the condensation of a primary amine with a carbonyl compound. These bases are active, well designed and stable under a variety of oxidative and reductive conditions [6]. The Schiff base of 4-aminoantipyrine having a pyrazoline skeleton and its complexes have a

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970903305437

variety of applications in biological, clinical, analytical, and pharmacological areas [7–9]. Coordination chemistry of pyrazoline has also received attention, primarily due to biological implications. Much work has been done [10–14] on the complexation of pyrazoline skeleton with iron, cobalt, nickel, and copper.

Studies of Schiff bases used in chemotherapy are now attracting the attention of biochemists [15, 16]; some drugs showed increased activity when administered as metal complexes rather than as organic compounds [17, 18].

Traditionally, Schiff bases are prepared by refluxing mixtures of the amine and the carbonyl compound in an organic solvent, for example, ethanol or methanol [19] and metal complexes by refluxing Schiff bases and metal salt in ethanol or methanol for several hours. Herein, benign, simple, cost-effective, and versatile routes to a Schiff base and its metal complexes are demonstrated. We investigate the synthesis, characterization, and comparison of the Schiff base derived from 4-aminoantipyrine as shown in figure 1 and its complexes by traditional and microwave-induced organic reaction enhancement (MORE) synthesis. In general, the reactions are very clean, without any side product. In fact, the crude products obtained are of high purity with remarkable yields and do not require chromatographic separation.

2. Results and discussion

The Schiff base 1-(2-furyl)-3-(4-aminophenyl)-2-propene-1-one (FAPPO) was prepared by the condensation of 4-fluoro benzaldehyde and 4-aminoantipyrine in ethanol classically and without using solvent ethanol under MORE technique as shown in scheme 1. The transition metal complexes were then synthesized by the reaction of

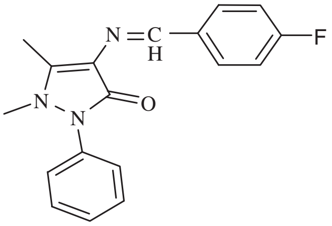
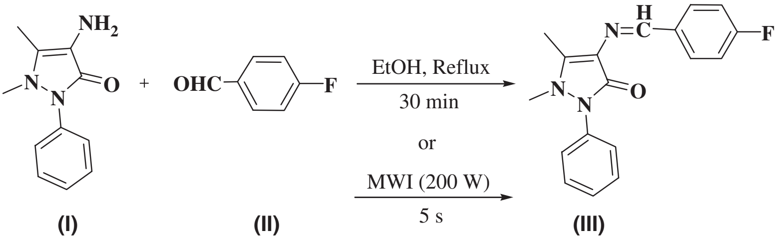


Figure 1. Ligand (FAPPO).

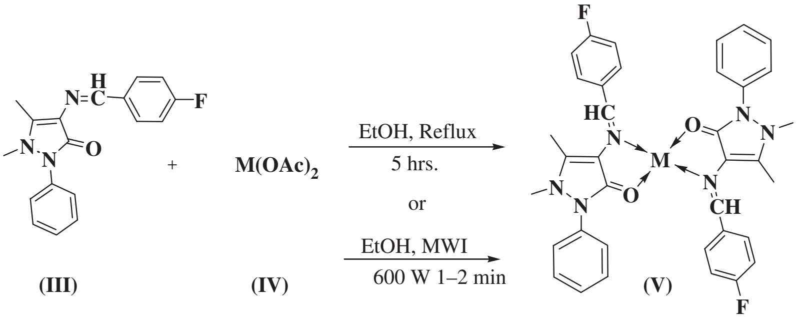


Scheme 1. Ligand synthesis.

appropriate metal(II) salts with ligand traditionally and by MORE as shown in scheme 2. The newly synthesized compounds were characterized by elemental analysis, ^{1}H-NMR, mass, UV-Vis and FTIR spectroscopy and X-ray diffraction studies. The data show that these complexes, ML_2, are air-stable, nonhygroscopic, colored solids, insoluble in water, and common organic solvents (alcohol, ethyl acetate, hexane, ether, and toluene) and soluble in dimethyl sulfoxide (DMSO) and dimethylformamide (DMF). Physical characterization and comparative yield data of ligand and complexes together with some physical properties are summarized in table 1. It is clear from the data that the MORE technique for the synthesis of the complexes is high yielding, easy, convenient, and ecofriendly as compared with the traditional method.

2.1. *Mass spectra*

The mass spectra of the ligand (FAPPO) and its metal complexes recorded at room temperature were used to compare their stoichiometry composition. The Schiff base showed a molecular ion peak at 309. The molecular ion peak for the nickel complex observed at *m*/*z* 676 confirms the stoichiometry of metal chelates as ML_2 type, also supported by mass spectra of other complexes.



M = Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Hg(II), and Sn(II)

Scheme 2. Complex synthesis.

Table 1. Physical characterization and comparative yield of ligand and complexes.

				TM		MT	
Compound	Molecular formula	Color	M.P	Time (h)	% Yield	Time (s)	% Yield
FAPPO	$C_{18}H_{16}FN_3O$	Orange	120	1.0	85	5.0	95
Zn(FAPPO)$_2$	$C_{36}H_{32}F_2N_6ZnO_2$	Orange	>250	5.0	80	15.0	90
Co(FAPPO)$_2$	$C_{36}H_{32}F_2N_6CoO_2$	Red	>250	5.0	83	25.0	95
Cu(FAPPO)$_2$	$C_{36}H_{32}F_2N_6CuO_2$	Orange	>250	5.5	81	18.0	92
Ni(FAPPO)$_2$	$C_{36}H_{32}F_2N_6NiO_2$	Green	>250	5.0	76	20.0	90
Hg(FAPPO)$_2$	$C_{36}H_{32}F_2N_6HgO_2$	Orange	>250	5.0	83	25.0	94
Sn(FAPPO)$_2$	$C_{36}H_{32}F_2N_6SnO_2$	Yellow	>250	5.0	85	35.0	95
Mn(FAPPO)$_2$	$C_{36}H_{32}F_2N_6MnO_2$	Yellow	>250	5.5	78	25.0	88

Table 2. Infrared spectral data (cm^{-1}) of ligand and complexes.

Compound	(C=O) pyrazolone	(C=N) azomethine	M–O	M–N
FAPPO	1650	1590	–	–
$Zn(FAPPO)_2$	1602	1550	455	392
$Co(FAPPO)_2$	1600	1552	450	382
$Cu(FAPPO)_2$	1600	1565	455	390
$Ni(FAPPO)_2$	1600	1562	472	365
$Hg(FAPPO)_2$	1600	1550	460	360
$Sn(FAPPO)_2$	1600	1550	465	365
$Mn(FAPPO)_2$	1602	1552	445	350

2.2. *IR spectra*

The IR spectra provide valuable information regarding the nature of functional group attached to the metal (table 2). Infrared absorptions of FAPPO have been assigned by comparison of its spectra with those of the pyrazole ring system [20], the monosubstituted benzene ring system [21], antipyrine, and 4-aminoantipyrine [22, 23], substituted 4-aminoantipyrine [24] and other Schiff bases of 4-aminoantipyrine [25, 26]. The infrared spectra of all the complexes show a considerable negative shift in carbonyl (pyrazolone) absorption (C=O) 45–50 cm^{-1}, indicating coordination through the oxygen. Another important band at 1590–1550 cm^{-1} attributed to (C=N) mode [27, 28] is shifted to lower frequencies in the spectra of the complexes (1570–1520 cm^{-1}) indicating –C=N coordination to the metal. Strong bands at 1510–1490 cm^{-1} assigned to ring stretching of the five-membered ring and several other absorptions associated with C–H out-of-plane deformation modes at 920–720 cm^{-1} undergo a slight positive shift due to decrease in electron density on the aromatic ring on complexation. Bands in the 460–360 cm^{-1} range are assigned to (M–O) and (M–N) modes (table 2).

2.3. *^{1}H-NMR spectra*

The ^{1}H-NMR spectrum of the ligand recorded in $CDCl_3$ are listed in section 3 and a table in "Supplementary material".

2.4. *UV-Vis spectra*

The UV-Vis spectra of FAPPO and complexes were recorded at room temperature in DMF. The electronic spectral data of ligand and complexes are given in "Supplementary material". The spectrum of FAPPO exhibits three main peaks at 370, 325, and 270 nm. The first and second peaks are attributed to aromatic π–π^* and imino π–π^* transitions, respectively. In the complexes blue-shift is observed in the bands indicating coordination of the imino nitrogen to metal. Further d–d transition of the complexes showed a broad band centered at 550–600 nm suggesting an approximate square planar geometry of the ligand around the metal ion. In the Ni-complex the main peaks are at 395, 340, 255, and 535 nm due to d–d transition assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1B_{2g}$ characteristic of square planar complexes.

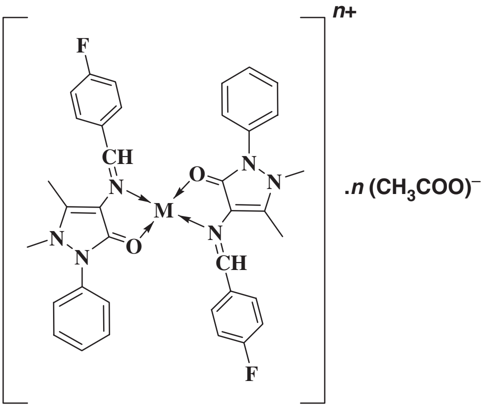


Figure 2. Proposed structure of complexes, where M = Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Hg(II), and Sn(II).

2.5. *Molar conductivities of the complexes*

Conductivity measurements in DMF for 10^{-3} M solution, table 3, show that the complexes are electrolytes. Thus, CH_3COO^- is present and completes the coordination sphere. On the basis of physical and spectral data, the structure in figure 2 is proposed for the complexes.

2.6. *X-ray diffraction studies*

The X-ray diffractograms of FAPPO and its metal complexes support that FAPPO has higher crystallinity than its complexes.

3. Experimental

Reagents such as 4-aminoantipyrine, 4-fluoro benzaldehyde, and various metal(II) acetates from Merck (USA) were used without purification. Anhydrous grade ethanol and DMF were purified according to standard procedures. FTIR spectra were recorded using KBr pellets on a Shimadzu spectrophotometer from 400 to 4000 cm^{-1}. A Perkin–Elmer Lambda 7 (UV-Vis) spectrophotometer was used to determine electronic spectra from 200 to 800 nm in DMSO. ^{1}H-NMR spectra of the Schiff base and metal complexes were recorded in DMSO-d_6 using a Varian XL-200 NMR spectrophotometer with tetramethylsilane as an internal standard. Mass spectra were recorded on a Varian MAT CH-5 spectrometer. Elemental analyses were carried out using a Perkin–Elmer, CHNS/O elemental analyzer model 2400. X-ray diffraction data were collected on PAN analytical Xpert-pro.

3.1. *Synthesis of the Schiff base ligand 4-(4-fluorobenzylidineamino)-1,2-dihydro-2, 3-dimethyl-1-phenylpyrazol-5-one by classical method*

Schiff base was prepared from the reaction of 4-aminoantipyrine and 4-fluorobenzaldehyde using a standard condensation protocol [22]. In the process, ethanol solution of

4-fluorobenzaldehyde 1.0 mm was added to the well-stirred solution of 4-aminoantipyrine 1.0 mm in ethanol. The reaction mixture thus obtained was refluxed for 30 min. The resulting reaction mass was allowed to attain room temperature. The yellow crystalline solid obtained was then filtered and washed with cold ethanol. It was dried and recrystallization was afforded by methanol.

3.2. *Synthesis of the Schiff base ligand 4-(4-fluorobenzylidineamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one by MORE method*

4-(4-Fluorobenzylidineamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one was obtained by the condensation of 1.0 mm of 4-aminoantipyrine and 1.0 mm of 4-fluorobenzaldehyde without solvent. In a typical preparation, the mixture of amine and 4-fluorobenzaldehyde were taken in a flask capped with a funnel, placed in a microwave oven and irradiated at 200 W for 5 s. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was allowed to attain room temperature. After cooling, the resulting solid was crushed, washed with cold ethanol, filtered, and dried under vacuum to give the crude product which was recrystallized using hot methanol.

3.3. *Synthesis of metal complexes [M (FAPPO)$_2$] by classical method*

Metal(II) complexes were prepared by addition of 1 mm of hot ethanol solution of $Zn(CH_3COO)_2 \cdot 2H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $Hg(CH_3COO)_2$, $Mn(CH_3COO)_2$, $Sn(CH_3COO)_2$, $Ni(CH_3COO)_2 \cdot 4H_2O$, or $Co(CH_3COO)_2 \cdot H_2O$ into a hot ethanolic solution of 1 mmol of FAPPO. The mixture was then refluxed for about 5 h. The precipitated solids were filtered from the hot ethanol reaction mixture, washed with hot ethanol and then with diethyl ether, followed by drying in an oven.

3.4. *Synthesis of metal complexes [M (FAPPO)$_2$] by MORE method*

Slurry of ligand (FAPPO) was prepared in aqueous ethanol. To this, a solution of metal acetates in ethanol was added. The resulting mixture was irradiated in a microwave oven for 1.0–2.0 min at medium power level (600 W) maintaining the occasional shaking. The hot reaction mixture was filtered, washed with hot ethanol and ether, followed by drying in an oven.

4. Conclusion

Coordination chemistry of a Schiff base obtained from the reaction of 4-aminoantipyrine and 4-fluoro benzaldehyde with Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Hg(II), and Sn(II) is described by traditional and MORE methods. The observed yields and improvement in reaction rates for this greener approach is attributed to the reaction conditions coupled with the use of microwave radiation. MORE method for the synthesis of complexes is convenient, high yielding, and ecofriendly as compared to the traditional method.

Acknowledgement

Financial support from University Grant Commission, New Delhi, is highly acknowledged.

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