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A Convenient Approach to the Synthesis of Different Types of Schiff's Bases and Their Metal Complexes

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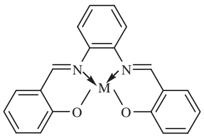
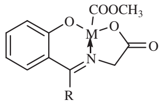
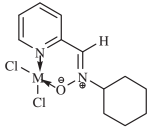
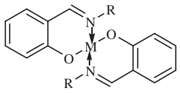
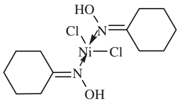
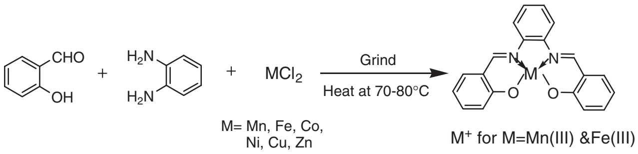
Various metal complexes derived from different Schiff bases are conveniently prepared using solvent-free condensation reactions in one-pot synthesis, resulting in significantly enhanced yields. Initial calorimetric studies, and/or TGA of reaction mixtures, led to better optimization of reaction conditions. The ligands like imines, hydrazones, semicarbazones, and nitrones are also synthesized by this method; thus this process is general and expedient.

Table 1. Comparison of reaction time and percentage yield of metal complexes synthesized in solvent (a) and under solvent-free condition (b)

Entry	Metal complex	Reaction time		Reported yield /%
		(a)	(b)	
1		1 h[7]	20 min	70–90
2		1 h[8]	20 min	75
3		6 h[9]	30 min	90
4		4 h[10]	30 min	50–60
5		2 h[10]	30 min	60–70



Scheme 1. An efficient one-pot synthesis of metal salphen complexes under solvent-free conditions.

One-pot multicomponent syntheses have received increasing attention of late, because they not only address fundamental principles of synthetic efficiency and reaction design, but they also expand the possibilities for extending the reactions into combinatorial and solid-phase methods.[1] The time has now come for ecological factors to be considered in the development of synthetic procedures and for them to play an important role in the assessment of the quality of any new synthesis. One simple approach to these issues is to perform reactions in the absence of solvents.[2–6] Thus a one-pot solvent-free condition for the preparation of different Schiff's bases and their metal complexes offers the distinct advantages of reduced reaction time and easier procedures for workup.

Our approach has been to evaluate one-pot multicomponent synthesis under solvent-free conditions via a study of well-established metal complexation reactions of various Schiff bases like salphen, imines, oximes, semicarbazones, hydrazones, and nitrones. Salphen metal complexes have been widely used in applications for everything from catalysts to molecular recognition[7] because of their versatility, and amino acid Schiff base metal complexes are involved in a variety of biological processes such as catalysis of transamination, racemization, and carboxylation reactions.[8] The synthesis and reactivity of some of these complexes, like those of nitrones,[9] have been playing an important part in the development of coordination chemistry. Typically the synthesis employs the use of organic solvents such as toluene or methanol, refluxing for over an hour, followed by extensive recrystallization and/or chromatography. Moderate yields are recorded in such processes.[10]

We have found that these complexes can be synthesized via a three component reaction sequence without using solvents. In this method, salphen and other Schiff's base derived metal complexes have been synthesized in significantly higher yields in a shorter time (Table 1). The same complexes were also prepared via solution phase, and comparisons have been listed in the table.

Synthetic details of salphen complexes are summarized in Scheme 1. In a typical experiment, the metal imine Schiff base complex is formed in near quantitative yield by grinding one molar equivalent each of the diamine and the metal acetate or chloride and two molar equivalents of the aldehyde using a pestle and mortar over a period of ca. 10 min. Heating the reaction mixture in an oil bath for further 20 min is followed by formation of the product as a colored solid.

Initially for optimization of reaction conditions, thermal gravimetric analysis (TGA) of a three component reaction mixture involving 1,2-phenylenediamine, salicylaldehyde, and a metal ion leading to the salphen metal complex was done. The thermal analysis was particularly useful in determining the minimum temperature at which the condensation reaction occurred as the onset of the reaction is found to be accompanied by the loss of molecule(s) of water. Thus the optimized time for the reaction is evaluated. This practice dramatically shortened the reaction time, and it is observed that the yield is almost quantitative. Moreover, the TGA[13] shows initial formation of ligand precursors followed by metal complexation, indicating

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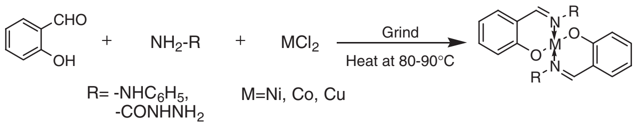
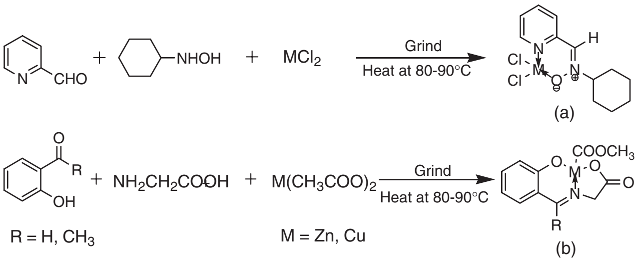


Scheme 2. An efficient one-pot synthesis of metal Schiff base complexes under solvent-free conditions.



Scheme 3. An efficient one-pot solvent-free synthesis of metal complexes of (a) nitrones and (b) hydroxybenzylideneglycine.

apparently that metal ions do not have any significant effect in the reaction system in solid phase. To further expand the scope, the new method stated herein was also applied to the synthesis of a number of other Schiff base metal complexes, details of which are summarized in Scheme 2. As a general approach one molar equivalent of the metal salt, two molar equivalents each of sodium acetate and the corresponding hydrochloride salt of hydroxylamine, hydrazine, or the semicarbazide were mixed together with a mortar and pestle. Aldehyde was then added to the reaction mixture.

Since only a few complexes of metals with simple nitrones have been reported, the versatility of this solventless method was also demonstrated by the facile formation of metal nitrone complexes and metal complexes derived of hydroxybenzylideneglycine, the synthetic plan of which are summarized in Scheme 3.

In a separate experiment, the ligand precursors of all the metal complexes were also synthesized in a convenient way under solvent-free conditions in lesser time, and quantitative yield is observed. For optimization of reaction conditions, DSC of a reaction mixture leading to the formation of a nitrone ligand precursor was done as shown in Figure 1.

Overall, this approach results in a dramatic improvement in yield in addition to the reduction in reaction time as compared to conventional methods involving organic solvents. The results of conductivity measurements carried in DMSO show that all the metal complexes are nonelectrolytes.[11] A typical cyclic voltammogram of Co(II)–salphen in DMSO was also obtained. The voltammetric characteristics of Co(II)–salphen and the magnetic moments of the metal complexes are found to be in good agreement with the literature data.[7,12] All the compounds are characterized[13] using IR, MS, and NMR data. The powder X-ray diffraction data of a few representative metal complexes have been done. A perfect match in the XRD data of the compounds are observed with that synthesized in solvent as shown in Figure 2.

We envisage the application of this strategy could be extended to prepare a wide range of Schiff base and related metal complexes. The method is partly mechanochemical and is useful in mimicking reactions done using high intensity grindings in ball mills and will score over other methods for its simplicity and easy reaction setup.

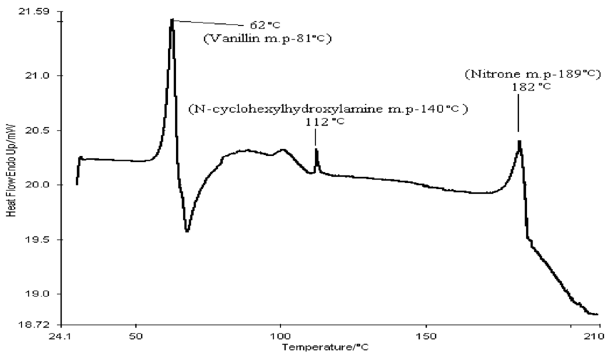


Figure 1. DSC data of nitrone formation in a reaction mixture.

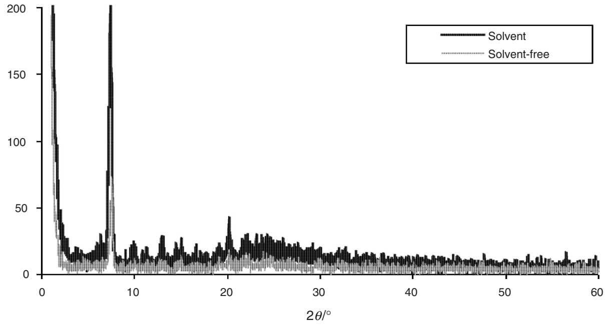


Figure 2. Comparison of Zn(II)–salphen synthesized in solvent and under solvent-free condition using powder X-ray diffraction.

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