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A Convenient Method to Synthesis and Characterization of Ni(II) and Zn(II) Schiff Base Complexes

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Abstract:

We have synthesized the schiff base and two metal-organic coordination compounds: $[Ni(C_{28}H_{18}N_2O_2)]$ complex 1 and $[Zn(C_{28}H_{18}N_2O_2)]$ complex 2, using liquid-assisted mechanochemical grinding (LAG). The compounds were characterized by infrared, X-ray Powder Diffraction, Energy dispersive x-ray, Differential scanning calorimetry and Thermogravimetric analysis, in all the complexes formed, the ligand coordinated with the metal ion through the two nitrogen atoms of the azomethine group (-N=C-) and two phenolic oxygen atoms of the schiff base to complete square planar geometry. The melting point, colour and X-ray diffraction patterns of the complexes were different from that of the schiff base ligand suggests formation of coordination compounds.

Keywords: Coordination compound, Azomethine, Schiff base, Complexes

1. Introduction

Recently, there has been a considerable interest in the chemistry of diamine-type schiff base complexes because of their potential for biological mimics (Jones, *et. al.*, 1979). Several reports on synthesis of metal complexes of diamine schiff base using organic solvents under reflux and their biological properties have already been published. More so, these methods suffer several drawbacks such as long reaction time, an excess of organic solvent, lower products yield and harsh refluxing conditions. Therefore, it is necessary to develop more efficient and versatile method for the preparation of schiff base metal complexes of aromatic diamine and the progress in this area is remarkable, including the use of liquid-assisted mechanochemical grinding (LAG). This method required the need of little solvent to derive the reaction which leads to new environmentally benign procedures that save resources and energy. Liquid-assisted mechanochemical reaction promises to be an essential facet of "Green Chemistry" and is of high interest from both the economical and synthetic point of view. LAG reactions possess some advantages over traditional reactions in organic solvents, for example they do not only reduce the burden of organic solvent disposal, but also enhance the rate of many inorganic reactions. Mechanochemical synthesis is the use of a mortar and a pestle or the more reproducible use of a ball-mill to grind the starting material in order to generate a complex series of structural transformations due to the vibrational effects caused by grinding of the reactants (two solid substances). Recent reports on the usefulness of mechanochemical synthesis was described by Kaupp 2009 via grinding a schiff base derived from benzaldehyde and sulphonamide with metal salts of Cu(II), Ni(II) and Co(II) to give neutral complexes of configuration $[M(L)_2 \cdot (H_2O)_2] \cdot Cl_2$. Marina *et. al.*, (2016) reported the synthesis of nine schiff base ligands derived from O-hydroxyaldehydes (2-hydroxybenzaldehyde, 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-1-naphthaldehyde) and nine corresponding dioxomolybdenum(VI) complexes, *cis*- $[MoO_2L(CH_3OH)]$ or *cis*- $[MoO_2L(CH_3OH)] \cdot CH_3OH$ and dinuclear $[MoO_2L]_2$, using the conventional solution-based method as well as mechanochemically, by liquid-assisted grinding (LAG). Kurawa and Yammama, (2014) reported the solid-state synthesis, characterization and antimicrobial study of 4,4'-bipyridine tetrachloronickelate (II) and 4,4'-bipyridine dichloronickel (II) complexes. The complexes were synthesized by grinding nickel(II) chloride with protonated 4,4'-bipyridiniumchloride. Dominik and Branko (2011), also reported the synthesis of schiff base ligand derived from 2-hydroxy-1-naphthaldehyde, namely 1-[(2-biphenylamino) methylen] naphthalen-2(1H) and its corresponding Cu(II) and Co(II) complexes using liquid-assisted grinding and characterised by means of IR spectroscopy, thermal analysis and also by powder and single crystal X-ray diffraction. In order to broaden the scale of investigations on schiff base and metal complexes, we have now synthesized, structurally characterized a schiff base derived from 2-hydroxy-1-naphthaldehyde and 1,2-phenylenediamine and its Ni(II) and Zn(II) complexes by liquid-assisted grinding.

2. Material and Method

Grinding in all the reactions was carried out in agate mortar with pestle. Chemical used in this study were obtained from Sigma Aldrich UK in >95% purity. All materials were used as obtained without further purification.

2.1. Synthesis of Schiff base: [H₂(L)]

2-hydroxy-1-naphthaldehyde, 2mmol (0.3444g) and 2-phenylenediamine 1mmol (0.1081g) of were weighed in to agate motor, a small amount of DMF (0.1-0.2ml) was added to allow the formation of paste during grinding and the mixture was ground for 30min to obtained light brown powder. The solvent was removed from the resulting paste of product by allowing it to stand for some time in the air.

2.2. Synthesis of Ni(II) Complex: [Ni(L)]

[H₂(L)] schiff base (1mmol, 0.4164g) and Nickel acetate tetrahydrate (1mmol, 0.2488g) were weighed in to agate motor, a small amount of DMF (0.1-0.2ml) was added and the mixture was ground for 30min to obtained light orange powder. The solvent was removed from the resulting paste of product by allowing it to stand for 12h in the air.

2.3. Synthesis of Zn(II) Complex: [Zn(L)]

[H₂(L)] schiff base (1mmol, 0.4164g) and Zinc acetate dihydrate (1mmol, 0.2195g) were weighed in to agate motor, a small amount of DMF (0.1-0.2ml) was added and the mixture was ground for 30min to obtained light yellow powder. The solvent was removed from the resulting paste of product by allowing it to stand for 12h in the air.

3. Results and Discussion

Compound	Molecular formula	Colour	Yeild (%)	Found (Calculated) (%)		
				C	H	N
[H ₂ (L)]	C ₂₈ H ₂₀ N ₂ O ₂	Light brown	88.6	81.13(80.75)	4.39(4.84)	6.44(6.73)
[Ni(L)]	C ₂₈ H ₁₈ NiN ₂ O ₂	Light orange	91.4	71.42(71.08)	3.17(3.83)	6.05(5.92)
[Zn(L)]	C ₂₈ H ₁₈ NiN ₂ O ₂	Light yellow	93.5	69.83(70.09)	3.92(3.78)	6.21(5.84)

Table 1: Physical properties of the schiff base ligand and its metal(II) complexes

Compound	v(C=N)	v(O-H)	v(C-H)	v(C-O)	v(C-C)	v(M-N)	v(M-O)
[H ₂ L]	1641	3396	3035	1215	1466	-	-
[Ni(L)]	1628	-	2913	1248	1489	684	473
[Zn(L)]	1621	-	2933	1296	1467	752	478

Table 2: Infrared spectral data of schiff base and its metal complex (cm⁻¹)

Compound	Element	Weight (%)	Atomic (%)	K Ratio	Line type
[Ni(L)]	C	59.72	66.40	0.01629	K Series
	N	15.87	15.13	0.00071	K Series
	O	21.26	17.74	0.00138	K Series
	Ni	3.15	0.72	0.00096	K Series
[Zn(L)]	C	60.30	67.92	0.03273	K Series
	N	13.95	13.47	0.00122	K Series
	O	20.79	17.58	0.00269	K Series
	Zn	4.96	1.03	0.00335	K Series

Table 3: Energy Dispersive X-ray (EDX)

Compound	Hydration tempt °C	%Weight loss: observed(calculated)	No. of H ₂ O of hydration	Melting point/decomposition tempt (°C)
[H ₂ (L)]	-	-	-	157
[Ni(L)]	-	-	-	278
[Zn(L)]	171	3.80(3.66)	1	177

Table 4: Thermal analysis of schiff base and its Complexes

The significant IR bands of the free schiff base ligand (H₂L) and their metal complexes were taken to detect the influence of a metal bonding on the ligand vibration in the complexes. In the FT-IR spectrum of schiff base, the strong band observed at 1641cm⁻¹ can be assigned to the -HC=N stretching vibration. The spectrum of schiff base also shows several bands corresponding to aromatic C-H stretching at 3035cm⁻¹, and aromatic C-C stretching 1466cm⁻¹ The absorption bands of the aromatic C-O and OH stretching vibration modes are centered at 1215 cm⁻¹ and 3396 cm⁻¹, respectively (Vadivela, and

Dhamodaranba 2015). In the spectra of Ni(II) and Zn(II) complexes, the -HC=N stretching vibration band is shifted to a lower wave number, 1628cm^{-1} and 1621cm^{-1} , respectively. This decrease indicates the coordination of the amino group nitrogen to the metal ion (Al-kubaiset. *al.*, 1994; Selwin *et. al.*, 2006). It is expected that coordination of nitrogen to the metal atom would reduce the electron density in the azomethine link and thus lower the -HC=N absorption. The O-H broad band in the schiff base was no longer found in the spectra of investigated metal complexes and also phenolic C-O stretching frequency in the Cu(II) and Ni(II) complexes was shifted to lower frequency in the region 1248 and 1292cm^{-1} respectively indicating deprotonation and coordination of the hydroxyl oxygen to the metal ion. (Reddy *et. al.*, 2006). $\nu(\text{M-N})$ and $\nu(\text{M-O})$ were observed in the far infrared region. These bands were absent in the spectra of the schiff base ligand. The $\nu(\text{M-N})$ of Ni(II) and Zn(II) were observed at 684 and 752cm^{-1} respectively as new bands in complexes. This occurrence indicates that there is coordination between the metal and the lone pair of electron on the nitrogen atom of the ligands. Also, bands observed at 478 and 473cm^{-1} , indicates the formation of M-O bond in Ni(II) and Zn(II) complexes respectively. (Nakamoto, 1997).

X-ray patterns of the schiff base, Nickel(II) and Zinc(II) complexes are recorded in the range of $5\text{-}40^\circ\text{C}$ (θ), the diffractogram and associated data depict the 2θ value for each peak relative intensity and inter-planar spacing (d-value). The patterns of the reactants compounds were completely different from the starting materials. Furthermore, no peak derived from the starting materials were observed, indicating that all starting materials were converted to product. The sharp reflections in the patterns testified to the crystallinity of the LAG products. Base on powder x-ray analysis data Zn(II) complex is more crystalline than Ni(II) complex. as shown in Figure 1

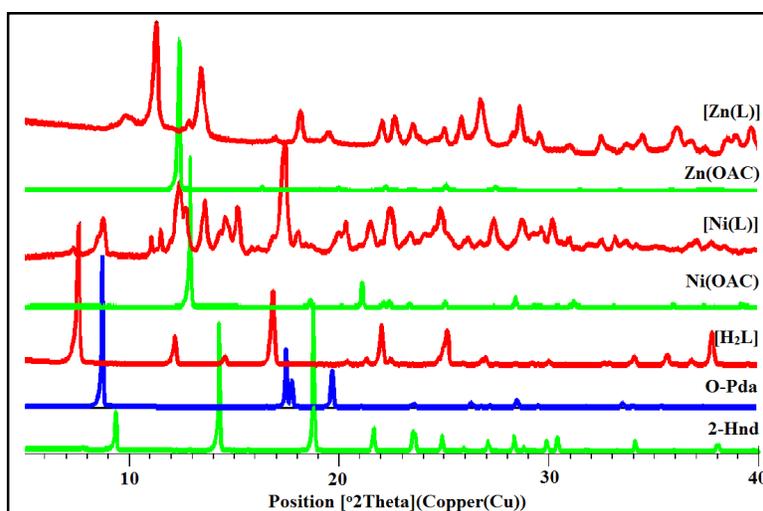


Figure 1: PXRD Patterns of pure 2-Hydroxy-1-naphthaldehyde (2-Hnd), pure 1,2-phenylenediamine (O-Pda), $[\text{H}_2\text{L}]$ schiff base, Nickel (II) acetate tetrahydrate (Ni(OAC)), $[\text{Ni}(\text{L})]$ complex, Zinc (II) acetate dihydrate (Zn(OAC) and $[\text{Zn}(\text{L})]$ complex product

EDX can be used to determine which chemical elements present in the sample, and can be used to estimate their relative abundance. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the samples being analyzed. Elemental mapping of a sample and image analysis are also possible as showed in figure. 2 and 3. EDX results of Ni(II) complex showed that, the atomic percentage of Carbon, Nitrogen, Oxygen and Copper are 66.40, 15.13, 17.74, and 0.72% respectively while that of Zn(II) complex were found to be 60.30, 13.95, 20.79, and 4.96% for Carbon, Nitrogen, Oxygen and Nickel respectively. (table 3). The atomic percentage of the component elements were compared in all the point analyzed and the results were found to be in agreement with each other indicating the uniform distribution of the component elements in the sample compound. Furthermore, the results are in conformity with the proposed structure of the complex.

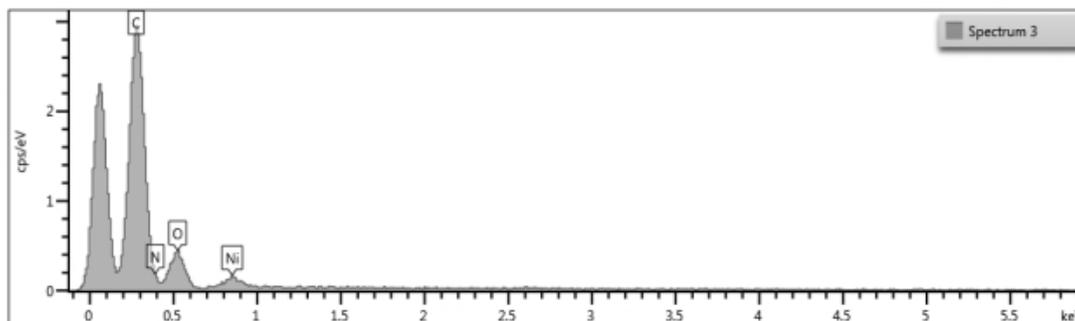


Figure 2: EDX analysis of $[\text{Ni}(\text{L})]$ complex showing peak due to Carbon, Nitrogen, Oxygen and Nickel in the complex compound

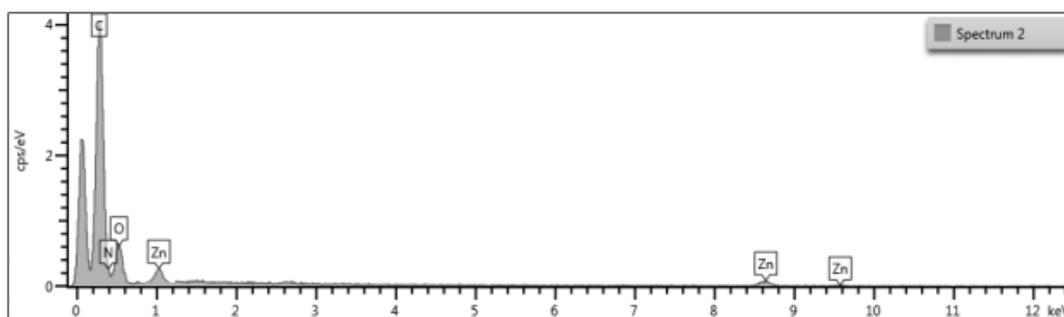


Figure 3: EDX result of [Zn(L)] complex indicating Carbon, Nitrogen, Oxygen and Zinc peak in the complex compound

Differential scanning calorimetry (DSC) curve of [H₂(L)] schiff base shows one endothermic peak at 126.3°C which corresponds to the melting point of the schiff base. TGA analysis of the metal complexes were studied from ambient temperature to 600°C under a nitrogen atmosphere. The curve of Ni(II) complex (Figure 4) displays no obvious weight loss at 170°C and exhibits one and relatively long decomposition step, decomposition starts at 278°C and complete at 410°C with weight loss of 58.0%, while for [Zn(L)] Complex exhibits a first estimated weight loss of 3.8% (calculated 3.66%) at 171°C (Figure 5) which is in agreement with loss of one water molecule, the first decomposition which is equivalent to 3% weight loss at 177-196°C, in the following stages within the temperature range from 196-363°C with weight loss 71.5%. The [Zn(L)] complex compound was obtained as powder product containing some amounts of residual water by-product as shown by TGA (Thermogravimetric analysis). However, on heating (105°C, 36h) complete loss of the water occurred to give a material with satisfactory elemental analysis.

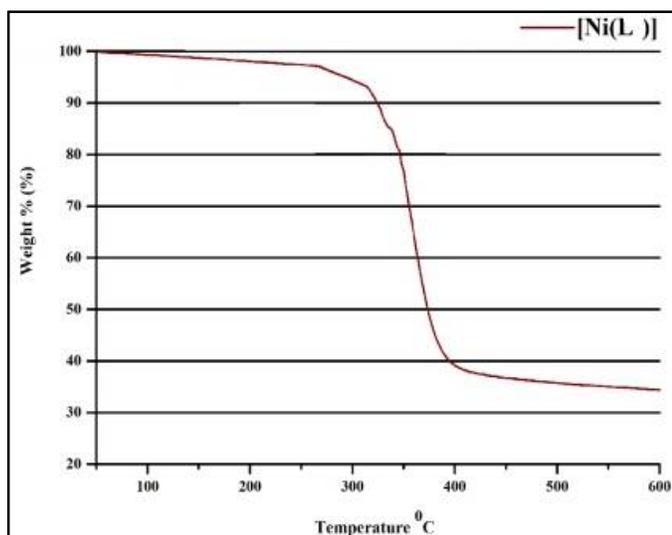


Figure 4: Thermogravimetric analysis of [Ni(L)] Complex

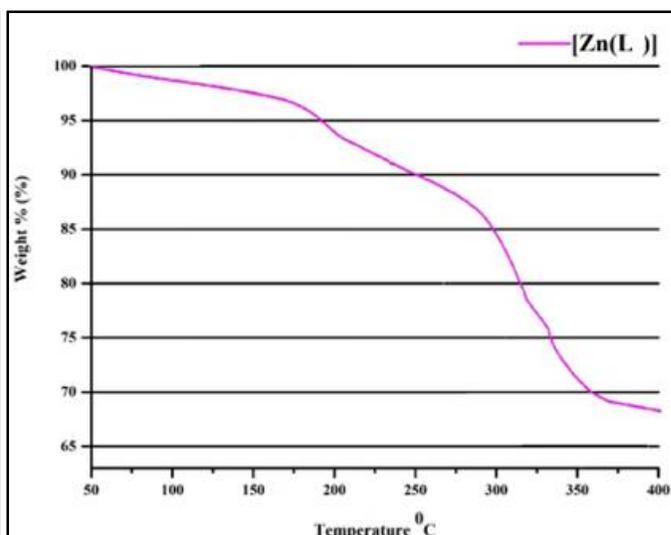
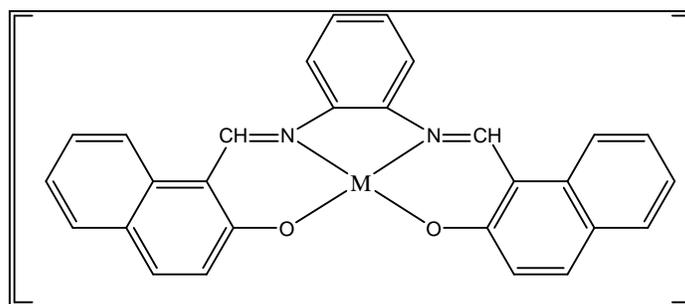


Figure 5: Thermogravimetric analysis of [Zn(L)] Complex

From the analyses of the schiff base metal (II) complex compounds carried out the general molecular structure is proposed as in Figure. 6



Where $M = Ni^{2+}$ and Zn^{2+}

Figure 6: Proposed molecular structure of complex

4. References

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