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Synthesis and Characterization of Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) Complexes with a New Unsymmetrical Tetradentate N_2O_2Schiff Base Ligand Driven from 2-Hydroxy-1-Naphthaldehyde and 3,4-Diamino-Benzoic Acid

Mohammad Taher Rezaee, Sayyed Javad Moafi[1*]

School of Chemistry, Damghan University, Damghan, Iran

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Abstract

Five mononuclear complexes containing a new unsymmetrical tetradentateN_2O_2Schiff base ligand are reported. The ligand, N,N'-bis-(2-hydroxy-1-naphthaldehyde)-3,4-diimino benzoic acid (**H_2L**), was synthesized from the reaction of 3,4-diaminobenzoic acid with 2-hydroxy-1-naphthaldehyde in the presence of glacial acetic acid in methanolic solution. The mononuclear Fe(**L**), Co(**L**), Ni(**L**), Cu(**L**), and Zn(**L**) complexes of the Schiff base ligand were synthesized from the reaction of the ligand with the metal salt in the solvent. The complexes were investigated by thermal and elemental analyses, molar conductance, and magnetic susceptibility measurements. Moreover, the ligand (**H_2L**) and its related complexes were characterized using ^{1}H NMR, IR, and UV-Vis spectroscopy. The results of undertaken examinations revealed all the metal complexes formed by the coordination of the N and O atoms of the ligand. Furthermore, the results of molar conductivity measurements indicated the complexes as non-electrolyte species in which the metal center bound to one **L^{2-}** ligand frame producing four-coordinate-species. Finally, the samples of nickel and zinc complexes were treated at high temperature up to 800 ^oC where their metal oxides were generated. XRD patterns and SEM images of the resulted oxides confirmed that these complexes might be appropriate entities for preparing nanoparticles.

Keywords: 2-Hydroxy-1-Naphthaldehyde, Schiff base, Co(II), Ni(II),nanoparticles, ZnO

1. Introduction

Schiff bases are amongst the most important classes of organic compounds which have been extensively studied in coordination chemistry [1-8]. Many Schiff base complexes have been used as catalysts in organic redox reactions and also as synthetic biological models in biological processes [9-13].Tetradentate Schiff base complexes with an N_2O_2 donor atom set are very well–known for coordination to inorganic metal ions giving rise to chelate adducts. From this point of view, unsymmetrical Schiff base complexes of

* [1]Corresponding author E-mail address: moafi@du.ac.ir Tel.: +98 23 35220095; fax: +98 23 35220095.

this type behave like many complexing agents in living organism [14-17]. Moreover, Quadridentate Schiff base M(II) ion complexes, particularly those of Co(II), have interested researchers for several decades due their ability to form reversible adducts with dioxygen [17-19]. A Schiff base ligand bearing a carboxylic group at the periphery of the coordinating moiety can be grafted on solid substrate containing appropriate covalently bound groups [20-22]. Recent researches have been focused on the preparation of such compounds, as these systems are expected to represent a specific behavior toward metal ions [22-24].

Despite intensive research on the reaction of various diamines with aromatic carbonyl groups, as far as our literature survey confirms, no report has yet been published on the synthesis of 3,4-diaminobenzoic acid with aromatic ketones. Besides, quite few works have been dedicated to the reactions of salicylaldehyde derivatives with the above mentioned diamine [20,25]. The main purpose of the present study was the synthesis and characterization of complexes containing a new tetradentate Schiff base.

In the present paper, we report the synthesis of a new unsymmetrical tetradentate N_2O_2 Schiff base ligand, **H_2L** and its metal complexes. The ligand has been synthesized from the condensation of 2-hydroxy-1-naphthaldehyde with 3,4-diamino benzoic acid. The Co(II), Ni(II), Cu(II), Zn(II) and Fe(II) complexes of this Schiff base ligand have also been prepared (Schemes 1 & 2). The ligand and its complexes have been investigated by elemental analyses, molar conductance, and magnetic susceptibility measurements at room temperature. Moreover, the compounds have been characterized using ^{1}H NMR, IR and UV-Vis spectroscopic techniques.

2. Experimental

2. 1. Materials and reagents

The following chemicals (reagent grade) have been used without further purification: $Ni(OAc)_2.4H_2O$ (Merck); $Zn(OAc)_2.2H_2O$ (Fluka); $Co(OAc)_2.4H_2O$ (Merck); $Cu(OAc)_2$.H2O (Merck); $Fe(SO_4).7H_2O$ (Aldrich); 3,4-diaminobenzoicacid (Alfa Aesar); 2-hydroxy-1-naphtaldehyd (Acros). The organic solvents including methanol, ethyl acetate, n-hexane, chloroform, diethyl ether, and dimethyl sulfoxide have been obtained from Merck and Fluka.

2. 2. Physical measurements

Infrared spectra have been measured from 400 to 4000 cm^{-1} as KBr pellets on a Perkin Elmer Spectrum RXI FT-IR spectrophotometer. ^{1}H NMR spectra have been recorded on a Bruker Avance DPX-400 spectrometer at 400 MHz and deuteriated dimethyl sulfoxide (DMSO-d_6) has been used as solvent. The electronic spectra in the 200–800 nm range have been recorded using DMSO solvent on a Perkin–Elmer Lambda 35 spectrophotometer. SEM images were obtained on a Hitachi S-4160 scanning electron microscope at an acceleration voltage of 30 kV. The samples have been attached to double-sided carbon tape and coated with 100 nm gold using a DC sputtering coater before capturing. Diffuse reflectance wide-angle XRD patterns have been obtained at room temperature with film specimens on a Bruker Avanced D8 X-ray diffractometer with Ni-filtered Cu/K alpha radiation [30 kV, 25 m A]. The melting points have been measured in capillary tubes using a Barnstead Electrothermal 9100 melting point apparatus. Elemental analyses were carried out by

Elementar Analysen systeme GmbH. The magnetic susceptibility measurements have been carried out for powdered samples on a Magnetic Susceptibility Balance Sherwood Scientific. The molar conductivity of the complexes have been determined in DMSO (10^{-3} M) at 27 ± 3 ºC using an Elico model conductivity meter.

2. 3. Synthesis of the unsymmetrical Schiff base ligand, N,N'-bis(2-hydroxy-1-naphthaldehyde)-3,4-diimino-benzoic acid, H_2L

In a typical experiment, a solution of 3,4-diaminobenzoic acid (1.52 g, 10 mmol) in absolute methanol (25 mL) containing a few drops glacial acetic acid was slowly added into a stirring solution of 2-hydroxy-1-naphthaldehyde (3.44 g, 20 mmol) in methanol (25 mL). The stirred mixture was refluxed for 20 hours to give a

yellow solution. The chemical reaction progress was monitored by TLC. The solvent was evaporated to about 15 mL with a rotary evaporator and the remaining was left undisturbed too cool down to room temperature. The light brown colored precipitate was then collected by gravity filtration and washed with cold methanol (3x10 mL) and chloroform and then dried under vacuum. Yield: 4.15 g, 90%. *Anal.* Calc. for $C_{29}H_{20}N_2O_4$: C, 75.65; H, 4.38; N, 6.08. Found: C, 75.54; H, 4.23; N, 6.19%. FT-IR (KBr, cm^{-1}) ν_{max}: (1595, 1623) (s, C=N), 1682 (s, C=O), 3338 (b, O-$H_{phenolic}$), 3420 (b, O-H_{acidic}). UV-visible (in DMSO) (λ_{max}, nm): 266 ($\pi\rightarrow\pi^*$), 310 ($\pi\rightarrow\pi^*$), 400 ($n\rightarrow\pi^*$). ^{1}H NMR (DMSO-d_6, δ ppm): 6.97-8.63 (15H, ArH), 9.70 (s, 1H_{imine}), 9.77 (s, 1H_{imine}), 14.80 (s, 2$H_{phenolic}$), 15.04 (s, 1H_{acidic}).

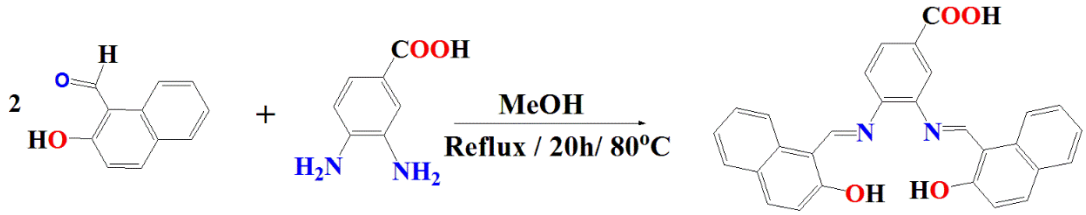
4. Synthesis of the metal complexes, M(L)

Unless stated otherwise, the Co(II),Cu(II), Ni(II), Zn(II) acetates and Fe(II) sulfate have been prepared according to the following procedure.

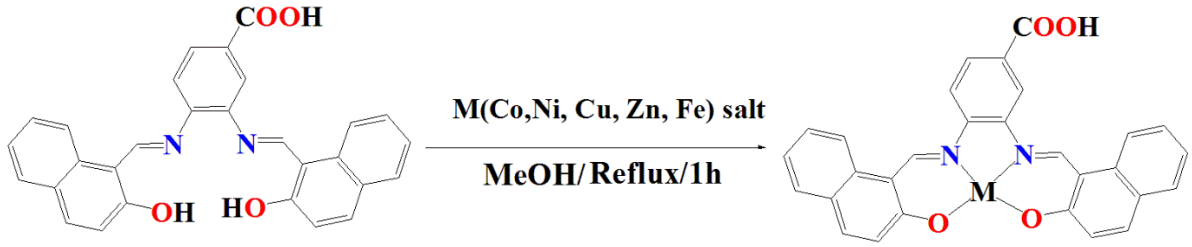
The ligand H_2L reacted with the corresponding metal(II) salt in methanol with immediate color change, to form non-electrolyte complexes M(L) [M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II)] in a suitable yield. The complex Co(L) has been prepared under nitrogen atmosphere. Analytical data of the metal complexes are compiled in Table 1.

3. 4. 1. Synthesis of N,N'-bis(2-hydroxy-1-naphthaldehyde)-3,4-diiminobenzoic acid nickel (II), Ni(L)

The dissolved Ni(II) acetate (1.708 g, 10 mmol) in methanol (20 mL) has been reacted with a methanolic solution (20 mL) of the Schiff base ligand, H_2L (4.605 g, 10 mmol) by 1-hour refluxing process (Scheme 2). After cooling, the precipitate has been separated by filtration and then completely washed with methanol. The product has been recrystallized from hot methanol, filtered and dried in vacuum. Yield: 5.66 g, 90%. *Anal.* Calc. for $C_{29}H_{18}NiN_2O_4$: C,67.35; H, 3.51; N, 5.42; Ni, 11.35. Found: C, 66.84; H,3.69; N, 5.23; Ni, 11.23%.FT-IR (KBr, cm^{-1}) ν_{max}: (1574, 1609) (s, C=N), 1678 (s, C=O), 3420 (b, O-H_{acidic}).UV-visible (in DMSO)(λ_{max}, nm):



Scheme 1. Synthesis of Schiff base ligand, *N*,*N'*-bis-(2-hydroxy-1-naphthaldehyde)-3,4-diimino-benzoic acid (**H_2L**)



Scheme 2. The overall synthetic procedure of the complexes,[M(**L**)] and the proposed structures of the Co(**L**), Ni(**L**), and Cu(**L**) complexes

270 ($\pi\rightarrow\pi^*$), 336 ($\pi\rightarrow\pi^*$), 396 ($n\rightarrow\pi^*$), 498 (CT). ^{1}H NMR (DMSO-d_6, δ ppm): 5.90-8.78 (15H, ArH), 9.43 (s, 1H_{imine}), 9.6`6 (s, 1H_{imine}), 15.15 (s, 1H_{acidic}).

3. Results and discussion

The Schiff base ligand, **H_2L** has been synthesized by a condensation reaction between 2-hydroxy-1-naphthaldehyde and 3,4-diamino-benzoic acid in a 2:1 molar ratio in methanol as shown in Scheme 1. The ligand **H_2L** has been coordinated to the metal ion center as a $N_2O_2^{2-}$ quadridentate moiety, through N and O sites to form 1:1 molar ratio species.

In order to synthesize the above mentioned ligand, a weak organic acid (acetic acid) was added to the aldehyde (2-hydroxy-1-naphthaldehyde) in a methanolic solution. The acid donated hydrogen ion to the carbon-oxygen bond of the keto form has yielded C=O-H^+ cation as a stronger electrophilic group. Then, the diamine (3,4-diamino-benzoic acid) wasadded to the mentioned solution and the mixture was refluxed for 20 hours. Note should be taken that no explicit product was detected in the absence of acetic acid even in DMSO solvent over several hours. The same reaction was also tried to be performed between the diamine and aromatic ketones but no reaction has been occurred.

As far as our literature survey showed, neither this specific reaction between 3,4-diamino-benzoic acid nor any carbonyl group has been reported. However, quite few reports with salicylaldehyde derivatives as formyl components have appeared in the literature in recent years [20, 24-25]. The ligand is stable at room temperature and soluble in polar organic solvents. The related complexes are also stable at room temperature and insoluble in water as well as most organic solvents except for DMSO and DMF. Based on the spectroscopic characterization, elemental analyses, magnetic susceptibility, and molar conductance measurements, the complexes have been recognized as non-electrolytes with four-coordinated environment. Analytical data of the ligand and its complexes are given in Table 1. As it is seen, the experimental elemental analyses are in good agreement with the theoretical calculations.

The molar conductivity measurements have been recorded for the metal complexes with 10^{-3} M solutions in DMSO at 25°C. The conductivity values for the complexes; Fe(**L**), Co(**L**), Ni(**L**), Cu(**L**), and Zn(**L**) have been in the range of 3-20 ($\Omega^{-1}cm^2\ mol^{-1}$) indicating that they all are non-electrolyte species. The above data confirms the complexation of 1:1 [metal: ligand] ratio of the formulate of [M(**L**)].

Since, single crystals of the complexes could not be isolated from any organic solution; no definite structure can be described. However, the spectroscopic and magnetic measurement data may lead one to predict possible structures of the complexes.

The magnetic susceptibility of the complexes was measured at room temperature and the magnetic moments were calculated and collected in Table 3. Co(**L**) effective magnetic moment value (μ_{eff} = 1.7 B.M.) is typical of low spin d^7 systems with one unpaired electron [26]. The obtained magnetic parameter is in accordance with a square-planar system. Therefore, dz^2 orbital of Co(**L**) forms electronic ground state containing the unpaired electron in such a system. Ni(**L**) complex is also a low spin (with d^8 configuration) diamagnetic moiety because its magnetic moment is almost zero. Therefore, the Schiff base ligand coordinates to Ni(II) ion as a four-dentate chelating agent with a square-planar environment. Similar situation may occur for Cu(**L**) complex due to its effective magnetic moment value (1.9 B.M.) indicative for a predominantly $d_{x^2-y^2}$ ground state occupied with one unpaired electron. Although, Co(II), and Ni(II) form low spin square-planar systems, Fe(**L**) with high spin d^6 configuration is expected to form a distorted square-planar environment [27].

3. 1. Elemental Analysis

The physical properties of the synthesized Schiff base ligand and its complexes are listed in Table 1. The results of the elemental analysis are in good agreement with the calculated values. The ligand has a specific melting point at 230°C but its complexes are decomposed just above 360-400 °C. All complexes are non-hygroscopic, stable in air, insoluble in water and most organic solvents, but they are easily soluble in DMF and DMSO. The results of analytical investigations show that these compounds are stable in air.

Table 1. Elemental analyses and physical properties of the Schiff base ligand and the metal complexes

Compound	Empirical formula	Formula Wt.	Color	$T_{m.p.}$* (ºC)	Yield (%)	Calculated (Found) % C	H	N	M**
H_2L	$C_{29}H_{20}N_2O_4$	460.46	Light brown	230	90	75.65 (75.54)	4.38 (4.23)	6.08 (6.19)	---
Fe(L)	$FeC_{29}H_{18}N_2O_4$	514.30	Black	360	75	67.73 (68.59)	3.53 (3.52)	5.45 (5.40)	10.86 (10.46)
Co(L)	$CoC_{29}H_{18}N_2O_4$	517.40	Dark brown	400	88	67.32 (66.94)	3.51 (3.59)	5.41 (5.62)	11.39 (11.23)
Ni(L)	$NiC_{29}H_{18}N_2O_4$	517.16	Red	390	90	67.35 (66.84)	3.51 (3.69)	5.42 (5.23)	11.35 (11.23)
Cu(L)	$CuC_{29}H_{18}N_2O_4$	522.00	Brown	380	85	66.73 (65.11)	3.48 (3.57)	5.37 (5.51)	12.17 (11.69)
Zn(L)	$ZnC_{29}H_{18}N_2O_4$	523.82	Dark yellow	370	85	66.50 (65.97)	3.46 (3.54)	5.35 (5.62)	12.48 (12.21)

* For complexes T_{dec} is expected. ** M = metal center

3. 2. Infrared spectra

The characteristic infrared spectral data of the Schiff base ligand and its complexes are given in Table 2. The complexes show similar IR spectral patterns. In order to study the ligand **H_2L** link to the metal ions in the complexes, the IR spectrum of the free ligand was compared with those of the complexes. The IR spectra of **H_2L** and its complexes exhibit significant differences.

In the IR spectrum of the ligand, a relatively broad band was observed at 3338 cm^{-1}, which may be contributed to the stretching vibrations of the phenolic O-H moieties. The absence of this band in the IR spectra of the complexes confirmed the dianionic nature of the ligand in the complexes [28]. The bands at 1595 and 1623 cm^{-1} in IR spectrum of the Schiff base ligand may be related to vibrations of the imine (C=N) groups.

Similar features have been monitored in the IR spectra of the complexes, the C=N stretching vibrations appearing in the 1570-1618 region (Table 2). The imine vibration is mostly shifted to lower wave numbers relative to the free ligand. The attached imine nitrogen in the complex accepts π-back bonding from the metal center to π* orbital of C=N group to decrease the imine bond order with respect to the free ligand [29]. In IR spectra of the complexes two more bands appeared in the range of 430-470 and 528-570 cm^{-1} which may be attributed to M-O and M-N stretching frequencies, respectively [30]. The band observed at 1682–1708 cm^{-1} in the IR spectra of all compounds is due to acidic (C=O) group vibration. The results of IR discussion are consistent with coordination of the ligand to the metal centers as a four-dentate $N_2O_2^{2-}$componentwith the specific integration, which is in accordance with the diamagnetic property of the complex. The pattern of ^{1}H NMR spectrum of the Ni(II) complex is similar to that of free ligand.

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

Compound	**ν(OH) phenol**	**ν(OH) acid**	**ν(C-H) aromatic**	**ν(C-H) imine**	**ν (C=O) acid**	**ν(C=N) imine**	**ν(M-N)**	**ν(M-O)**
H_2L	3338	3430	~ 3050	~ 2920	1682	1595, 1623	---	---
Fe(L)	---	3414	~ 3050	~ 2920	1696	1570, 1600	560	444
Co(L)	---	3414	~ 3050	~ 2920	1702	1576, 1618	528	442
Ni(L)	---	3420	~ 3050	~ 2920	1678	1574, 1609	570	430
Cu(L)	---	3412	~ 3050	~ 2920	1708	1576, 1608	560	470
Zn(L)	---	3418	~ 3050	~ 2920	1684	1578, 1616	554	450

3.3.^{1}H NMR spectra

The ^{1}H NMR spectra have been carried out in DMSO-d_6 solution to clarify the Schiff base ligand H_2L and its Ni(L) complex structures. The spectral data of the ligand and its Ni(L) complex are given in Section 2 and their spectra are shown in Figure 1.

The signals at around 15 ppm in the ^{1}H NMR spectra of the free ligand (H_2L) and the Ni(L) complexmay be attributed to the OH component of the acidic group. The other broadened signal exhibited at 14.80 ppm in the free ligand spectrum has been assigned to the phenolic OH protons. Moreover, pronounced upfield shift of the phenolic protons and its broadness is clearly due to strong intramolecular O-H⋯N hydrogen bonding effect [31]. This peak is completely disappeared in the spectrum of Ni(L) complex indicating that the OH protons have been removed by the chelation with Ni(II) ion. Signals of the N=CH imine protons have appeared at 9.70 and 9.77 ppm in the ^{1}H NMR spectrum of the ligand. The same peaks have been observed at 9.43 and 9.66 ppm in the spectrum of the complex. The two peaks undergo upfield shift due to coordination to the metal center. The aromatic protons have been exhibited in the range of 5.90-8.78 ppm

3. 4. Electronic spectra

The UV-visible absorption spectra of the ligand **H_2L** and its complexes were obtained in 10^{-4} DMSO solutions at room temperature (Table 3). The intense bands centered less than 360 nm, may be assigned to $\pi\rightarrow\pi^*$ transitions of the azomethine, benzoic acid, and naphthalene groups of the ligand. The other peak which has appeared in the 400 nm region of the ligand spectrum is attributed to $n\rightarrow\pi^*$ transition [32]. In the spectra of the related complexes, the bands due to the ligand ($\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions) are still pronounced with a tiny shift with respect to the corresponding bands in the free ligand. In addition, a charge transfer band at 483-500 nm has been also observed in the electronic spectra of the complexes [33].

Table 3. Molar conductivity, Magnetic moment, and electronic spectral data of the complexes

Complex	Solvent	Molar Conductance Λ_m (Ω^{-1} cm^3 mol^{-1})	μeff(B.M.)	d^n	λ_{max} (nm) $\pi\rightarrow\pi^*$	λ_{max} (nm) $n\rightarrow\pi^*$	λ_{max} (nm) C.T.	Suggested Geometry
Fe(L)	DMSO	16-20	5.10	d^6 (H.S.)	276, 344	413	480	Distorted S.P*.
Co(L)	DMSO	4-6	1.70	d^7 (L.S.)	273, 353	429	500	S.P.
Ni(L)	DMSO	4-5	~ 0	d^8 (L.S.)	270, 336	396	494	S.P.
Cu(L)	DMSO	3-5	1.90	d^9	280, 334	437	483	S.P.
Zn(L)	DMSO	5-7	~ 0	d^{10}	270, 332	424	482	S.P./Td**

* S.P. = Square planar, ** Td = Tetrahydron.

It should be mentioned that no d → d transition has been observed due to the presence of the intense charge transfer band in this region [33]. The Zn(**L**) complex with d^{10} electronic configuration had no d → d transition but still one band is detected at 482 nm in its spectrum. Therefore, this intense electronic transition is basically due to MLCT (metal to ligand charge transfer). As a result, the band at 483-500 nm in electronic spectra of the other complexes cannot be attributed to d → d transitions [32]. However, the intensity of absorption at visible region might have minor contribution to band intensity due to underlying d → d transitions.

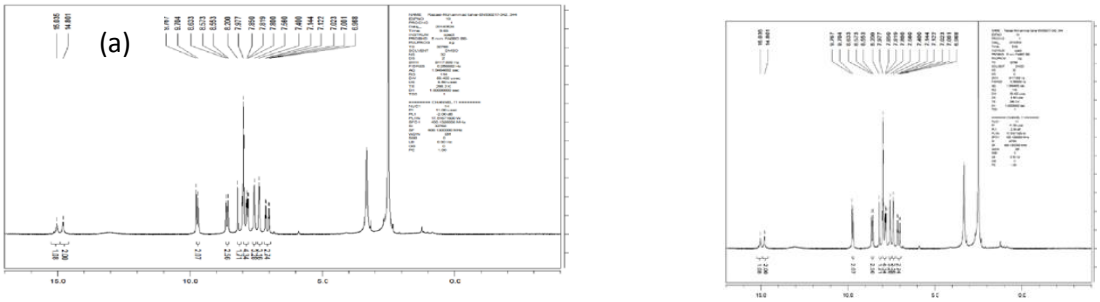


Fig. 1.^{1} H NMR spectrums of the Schiff base ligand (H_2L) (**a**) and its[Ni(L)] complex (**b**) in DMSOd_6

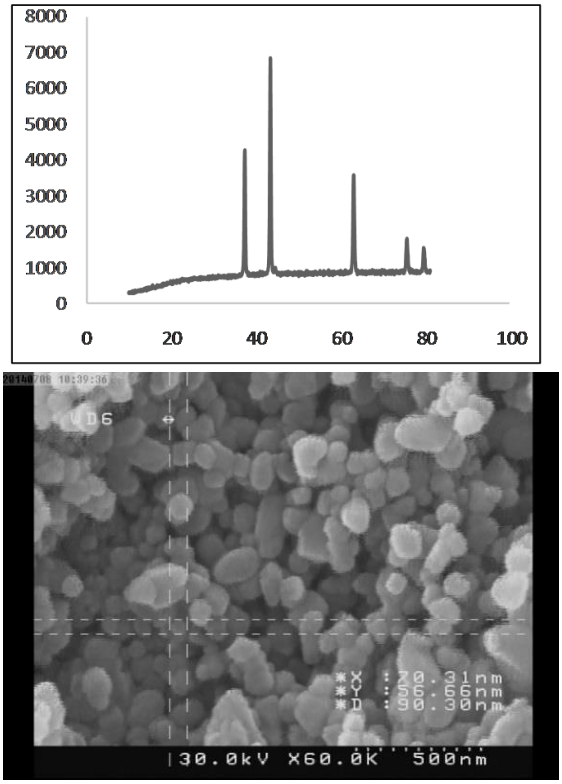


Fig. 2. XRD pattern (above) and SEM image (below) of NiO nanoparticles.

3. 5. Preparation of NiO and ZnO Nanoparticles

In last two decades, the transition metal oxide nanoparticles have been extensively utilized as an active catalyst in many reactions. Transition metal oxides nanostructures have a wide variety of surface structures which affect the surface energy of these compounds and also their chemical properties [34-35]. For instance, ZnO nanoparticle is unique among known nanocrystallites which have been used for the fabrication of solar cells, semiconductors, photoactivity, gas sensors, and antibacterial materials [34, 36-37]. To examine the products of decomposed complexes, a sample of Ni(**L**) and Zn(**L**) complexes have been separately placed into a crucible and kept in a furnace to heat at a rate of 10 ºC/min in air. In this process, nickel oxide and zinc oxide have been formed at 800 ºC after five hours.

The produced NiO and ZnO powders have been characterized by XRD and SEM. The XRD pattern of NiO exhibited the main diffraction peaks. The XRD patterns confirmed that the products were nickel oxide and zinc oxide and they are indexed to pure NiO cubic phase and ZnO hexagonal phase. The crystallite size diameter (D) of the nanoparticles has been calculated by Debye–Scherrer equation. The diameters of the nanoparticles were 40 nm and 28 nm for nickel and zinc oxide species, respectively. The surface morphological study and particle size of the NiO and ZnO nanoparticles have been also carried out using SEM images. The results of these two techniques show that small particles with approximately nano-sized, NiO and ZnO have been generated due to decomposition of the related complexes in air. The XRD pattern and SEM image of NiO nanoparticles are illustrated in Fig. 2.

4. Conclusion

A new unsymmetrical N_2O_2 type Schiff base ligand containing N,N'-bis-(2-hydroxy-1-naphthaldehyde)-3,4-diimino benzoic acid, has been synthesized from the reaction of 2-hydroxy-1-naphthaldehyde with 3,4-diimino benzoic acid. Moreover, its mononuclear Fe(**L**), Co(**L**), Ni(**L**), Cu(**L**), and Zn(**L**) complexes have been prepared and characterized. According to the analytical and IR spectral data, the mentioned complexes have been generated by the coordination of O and N atoms of the ligand. The geometrical structure around the Fe(II) center suggested as a distorted tetrahedron which strongly influenced by the nature of the high spin iron center. However, Co(**L**), Ni(**L**), Cu(**L**), complexes constructed square-planar species emerged mainly from the UV-Vis spectra and the magnetic moment calculations. Moreover, the present work demonstrated a facile synthetic route for the construction of highly dispersed metal oxide nanoparticles.

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