

Synthesis and Characterization of Metal Complexes of Derivative of 1,10-phenanthroline

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Mononuclear complexes of Zn(II) N,N' coordinated with phendione and phendioxime and polynuclear of Ni(II), Cu(II) and Zn(II) complexes of the phendioxime were synthesized and characterized by direct and template method. Ni(II), Cu(II) and Zn(II) species coordinated by N,N' of the oximate and phen groups, Ni(II) complex of the oximate has square-planar geometry and phen has octahedral geometry whereas; Cu(II) and Zn(II) complexes of oximate and phen have octahedral geometry. Mononuclear complex of Zn(II) with phendione N,N' coordinated was precursor for mononuclear complex of Zn(II) with phendioxime N,N' octahedral coordinated by phen group and heteronuclear complex of Ni(II) with mononuclear Zn-phendioxime complex was synthesized and characterized by template method. Zn(II) and Ni(II) species coordinated by N,N' of phen and oximate groups, respectively. Zn(II) moiety coordinated through N,N' of phen has octahedral geometry and Ni(II) moiety coordinated through N,N' of oximate has tetrahedral geometry. Structures of the ligand and its complex are suggested and formulated according to the elemental analysis, ¹H, ¹³C NMR, UV-Vis, IR, AAS, molar conductivity and magnetic susceptibility.

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1. INTRODUCTION

One of the major interests in coordination chemistry is to study the interaction of a central atom with surrounding atoms, ions or molecules. Vic-dioximes, have a great importance since they are used as chelating agents because they form stable complexes with transition metals, also they have been widely studied as analytical reagents. The chemistry of transition metal complexes with (E,E)-dioxime ligands is the subject of several reviews. The high stability of the complexes prepared with vic-dioxime ligands has been extensively exploited for various purposes, such as use as analytical reagents and as models for some biological systems; they are also useful as catalysts in many chemical processes or as templates in some organic reactions [1,2].

The coordination chemistry of vicinal dioximes is interesting and numerous transition metal complexes of this group of ligands have been investigated. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure, stabilized by hydrogen bonding [3].

Oximes have been widely recognized as ligands and in the meanwhile, purpose-designed compounds have received attention due to their potential technological applications. Oxime complexes have also been used as cerebral and myocardial perfusion imaging agents. Oxime complexes of rare-earth elements, especially uranium and lutetium, are of particular interest for their optical, conductive, mesogene and redox properties [4].

Vicinal dioximes have also been widely investigated as analytical reagents, compounds having columnar stacking are thought to possess

semiconducting properties and, recently in macrocyclization reactions [3]. Both the presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms make (E,E)-dioximes amphoteric ligands which form corrin-type square-planar, square-pyramidal and octahedral complexes with some transition metal ions such as Ni(II), Co(II), Cu(II), Pd(II) and Co(III) as central metal atoms [2].

The dioxygen binding ability of bis(dioximate) cobalt(II) complexes has been the focus of considerable attention in recent years and has been extensively involved in the design, synthesis and characterization of several classes of compounds that have been shown to reversibly bind dioxygen. The oximate group (=NO⁻) can function as a bridge between two metal ions through the imino nitrogen and the deprotonated oxygen, to yield bi and trinuclear complexes. Typical examples are mono-, bi and trinuclear Cu(II) complexes with a single or double oximate bridge arrangement (type B or C in Fig. 1). Synthesis of the C type (Fig. 1) trinuclear Cu(II) complex was first attempted by Singh and Sahoo using dimethylglyoxime and acetylacetonedioxime [3,5]. The study of the magnetic exchange interaction in polynuclearmetal complexes in terms of structural factors and, in view of the nature of the bridging groups, are continuing subjects in the field of coordination chemistry and is one of the most active research areas in magnetism [5].

This field is very important with respect to an understanding of fundamental factors governing the magnetic properties of transition metal compounds and finding appropriate systems applicable as building units to the design of new materials. This paper reports the synthesis methods and characterization of mononuclear Ni(II), Zn(II) and Cu(II) complexes derived from

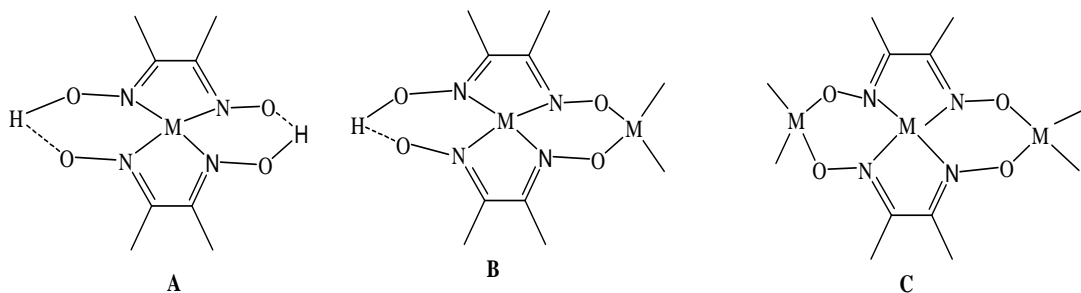


Fig. 1. Bridging groups of oximes

1,10-phenantroline-5,6-dione using direct method and polynuclear Zn-Ni(II) complexes using new template method. The synthesis and characterization are reported by NMR, UV-Vis, AAS and IR spectroscopies, magnetic susceptibility and molar conductivity of the mono, hetero and polynuclear complexes.

2. EXPERIMENTAL PART

All chemicals have above 99% purity and purchased from Sigma Andric. Melting points were determined using electrothermal IA 9200 Digital Melting Point Apparatus. The IR and far-IR spectra ($4000-650\text{ cm}^{-1}$) were recorded on a SHIMADZU FTIR-8400S spectrophotometer in KBr. The electronic (UV-Vis) absorption spectra were measured on a Spectronic GENESY'S 2PC UV-Vis spectrophotometer in the 200-800 nm regions. ^1H and ^{13}C -NMR were collected using Bruker Ultra-shield NMR (400 and 100.6 MHz for ^1H and ^{13}C , respectively). Molar conductivities were measured with JENWAY 4330 Conducting and pH meter using 10^{-3} M solution of each complex in DMSO at room temperature (22°C). The molar magnetic susceptibilities of powdered samples were measured using MSB-AUTO (Sherwood Scientific) at room temperature. Flame Atomic Absorption Spectrometer (BUCK MODEL SCIENTIFIC 210 VGB) was used to measure the amount of metals ($\mu\text{g/mL}$) in their prepared solutions. Elemental analysis was done using Exter Analytical CE 440 EA Elemental Analyser.

3. SYNTHESIS OF PHENDIONE (PD)

This compound was prepared according to a simple modification of the published procedure [6].

100 mL of 96% H_2SO_4 , 50 mL of 65-67% HNO_3 in 100 mL beaker and (10 g, 58 mmol) of phen and (10 g, 53 mmol) of KBr in dish were equipped in refrigerator overnight. H_2SO_4 and HNO_3 were mixed in a 200 mL beaker and transferred to separatory funnel. In a three-necked flask phen and KBr were taken. To this solid mixture the cooled acid was added from a dropping funnel very slowly. The red orange suspension was allowed to warm up to room temperature and heated at 150°C until the evolution of Br_2 had ceased (12h). The yellow suspension was cooled at room temperature and poured on ice. The pH of the mixture was carefully raised to 6 by addition of 30% NaOH (w/w). The yellow suspension was extracted with

CH_2Cl_2 . after drying with Na_2SO_4 . The solvent was removed in vacuo, at 40°C and the residue recrystallized from hot methanol (three times) obtaining as yellow needle powder. (Yield = 20% and mp = 160°C).

3.1 Synthesis of Ligand or Phendioxime (PDO)

This compound was prepared according to the published procedures [7-8].

A mixture of PD (0.21 g, 1.00 mmol) and Na_2CO_3 (0.296 g, 1.50 mmol) was taken in R.B flask and dissolved in ethanol (15 mL). This mixture was heated to reflux at 60°C . To this solution hydroxylamine hydrochloride (0.243 g, 3.5 mmol) dissolved in ethanol (5 mL) was added drop wise and the reaction mixture was then refluxed for 5 h. After completion of the reaction, the mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was washed successively with water and ether and dried in vacuum at 80°C obtained, as a light yellow powder. (Yield = 83% and mp = 200°C).

3.2 Synthesis of Metal Complexes Using Direct Method

The metal complexes were prepared by procedures reported in the literature [1-4].

3.3 General Procedure for the Synthesis of Ni(II), Cu(II) and Zn(II) Complexes

A solution of ligand (0.288 g, 1.2 mmol,) was prepared in ethanol (25 mL) in a R.B flask.

To this, a solution of metal chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.078 g, 0.6 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.085g, 0.5 mmol) and ZnCl_2 (0.82 g, 0.6 mmol)) in 25 mL of ethanol was added. The pH of the resultant solution mixture decreased to 3. As a result, the following colour changes were observed: (red-brown for Ni(II), black for Cu(II) and greenish-yellow for Zn(II)). pH was raised to 5 by drop wise addition of 1% NH_4OH solution in ethanol. A magnetic stirrer was introduced. The mixture was stirred while heating on hot water bath for 1h at $55-60^\circ\text{C}$. The metal complexes that were thus synthesized were filtered. They were washed with water, ethanol and diethyl ether and then dried at 100°C in vacuo. (Yield: Ni(II), 64.28%, Cu(II), 72% and Zn(II), 43.72%; mp: Ni(II), does not melt upto 337°C , Cu(II), 330°C and Zn(II), 332°C).

3.4 Synthesis of Metal Complexes Using Template Method

3.4.1 Synthesis of N,N'-Zn-PD complexes

This complex was prepared according to the published procedures [9].

The PD (0.210 g, 1 mmol) was weighted into R.B flask. It was dissolved in 30 mL ethanol. A solution of ZnCl₂ (0.136 g, 1 mmol) in 30 mL ethanol was prepared. It was added drop-wise to phendione solution. A magnetic stirrer was introduced. The mixture was stirred while heating on hot water bath for 1 h at 40°C for 20 h. The deep-green precipitate was collected by suction filtration and washed with ethanol and ether. (Yield: 20%, mp 305-307°C)

3.4.2 Synthesis of N,N'-Zn-PDO complexes

A mixture of N,N'-Zn-PD complexes (0.14 g,) and Na₂CO₃ (0.148 g, 0.75 mmol) were dissolved in ethanol (15 mL) and heated to reflux. To this solution hydroxylamine hydrochloride (0.13 g, 1.75 mmol) in ethanol (5 mL) was added drop wise and the reaction mixture was then refluxed for 5h. After completion of the reaction, the mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The light-yellow residue was washed successively with cold ethanol and ether and dried under vacuum at 80°C affording the complex, as a light yellow solid. (Yield = 96% and mp = 295°C).

3.4.3 Synthesis of N,N'-N,N'-Zn-Ni-PDO complexes

A solution of NiCl₂.6H₂O (0.08 g, 0.3 mmol) in 25 mL of ethanol was added to a solution of N,N'-Zn-PDO complexes (0.15 g) dissolved in 25 mL of ethanol taken in a R.B flask. The pH of the mixture changed to 6 and its colour turned to light-brown. In order to raise the pH to 7, 1% NH₄OH solution in ethanol was added and the mixture was heated on water bath at 60°C the mixture was stirred with a magnetic stirrer during thus heating for 1h. The dark-brown precipitate was filtered in hot condition, washed with cold ethanol and diethyl ether and dried at 100°C in vacuo. (Yield = 64.28, mp= does not melt up to 337°C).

4. RESULTS AND DISCUSSION

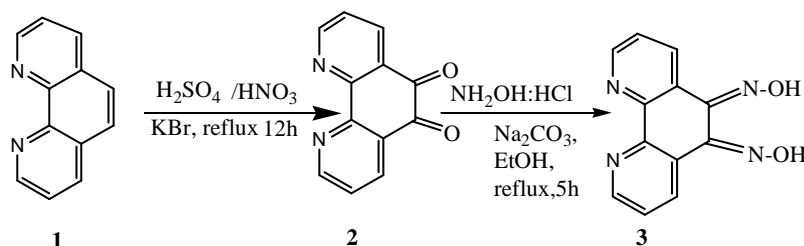
The synthesis of phendioxime (H₂L) and their mononuclear and binuclear complexes are

summarized in Scheme 1-2 and Figs. 2-3. The compounds are less soluble in polar organic solvents, such as CHCl₃, MeOH, and DMSO in nonpolar organic solvents, such as n-hexane, benzene and Et₂O. Furthermore, hot solution of the ligand was used during complexation. NH₄OH in ethanol were used in complexation to raise the pH of the solution, these shows formation of complexes. In general, reactions of the ligand with a metal salts were quick and gave a good yield of mononuclear and binuclear complexes corresponding to the general formula ML₂ and M₁M₂L₃.

The authentic of the ligands and their complexes have been established by NMR, IR, spectra, UV-Vis spectrum, magnetic susceptibility and conductivity measurements, AAS and chloride estimation and elemental analysis.

In the ¹H-NMR spectrum of phendione (2) (the NMR spectrum was obtained in CDCl₃) shows three doublets of doublet signals at δ 9.14, 8.53 and 7.62 ppm. The three non-equivalent signals are chemically environment six protons of the phendionering. The ¹³C-NMR. spectrum shows six signals which corresponds to at δ 178.67, 156.43, 152.92, 137.33, 128.08 and 125.63 ppm in the aromatic region. The six non-equivalent signals are due to the six types of non-equivalent carbons in the phendione ring. The DEPT spectrum also shows three signals at δ 156.46, 137.36 and 125.64 ppm for the three =C-H groups in the phendione ring and the signals at 178.67, 152.92 and 128.08 ppm disappeared which confirms that the three types of carbons are quaternary carbons. Hence both the ¹H and ¹³C NMR data supports the structure deduced. In the UV-Vis spectra of the ligands were taken in DMSO. In the UV-Vis spectrum of phendione (2) a band at 266 nm (37597 cm⁻¹) is assigned to π→π* transitions. Another band at and 292 nm (34247 cm⁻¹) has been assigned to n → π* transitions. In the UV-Vis spectrum of phendioxime (3) a band at 261 nm (38314 cm⁻¹) is assigned to π→π* transitions. Another band at 315 nm (31746 cm⁻¹) has been assigned to n→π* transitions. And the elemental analysis in Table 1 shows satisfactory correspondence to given structures of the ligands phendione (2) and phendioxime (3).

The mononuclear metal (II) complexes of the vic-dioxime, Fig. 3, I and II, were prepared in 65%, 72%, and 44% for Ni, Cu, and Zn metal complexes yields, respectively, by treating metal salts in an absolute ethanol mixture with the



Scheme 1. Synthesis of phendioxime

Table 1A. Elemental analysis and physical properties of ligands and complexes

Compounds	Color, appearance	Yield, %	Mp, °C	Found (Calculated)		
				C%	H%	N%
1 PD	yellow, needle	20	160	68.57 (68.21)	2.85 (2.82)	13.33 (13.23)
2 PDO	Light-yellow, powder	83	200	59.87 (60.0)	3.21 (3.33)	23.56 (23.33)
3 Ni-PDO	dark-brown, powder	64.28	>337	43.16 (43.24)	2.781 (1.95)	15.818 (16.88)
4 Cu-PDO	Black, powder	72	330	37.907 (38.55)	1.823 (1.74)	13.701 (14.99)
5 Zn-PDO	greenish-yellow, powder	43.72	332	37.34 (37.79)	1.93 (1.82)	13.44 (14.97)
6 N,N'-Zn-PD	Deep-green, powder	20	305- 307	51.79 (51.91)	2.15 (2.03)	10.07 (10.98)
7 N,N'-Zn-PDO	light-yellow, powder	96	295	51.14 (51.07)	2.85 (2.12)	10.00 (10.21)
8 N,N'-N,N'-Zn-Ni-PDO	dark-brown, powder	64.28	>337	39.13 (39.75)	2.17 (2.11)	7.60 (7.99)

Table 1B. IR and UV-Vis spectra of ligand and complexes

Compound	IR spectra (cm ⁻¹)			UV-Vis spectra (nm)		
	OH-	C=N	N-O	M-N	π→π*	n→π*
H ₂ L	3400-3100	1464	1070	-	-	-
NiL ₂	3300s	1459	1051	721	282	413
CuL ₂	3300w	1457	1045	721	288	419
ZnL ₂	3300w			721	280, 314	438
Zn-Ni-L ₃		1464		721	264	308, 350

ligand in the presence of a base NaOH in ethanol. Metal (II) complexes have a metal-ligand ratio of 1:2 according to the elemental analysis. The NMR spectrums due to poor solubility were not recorded. In the IR spectrum of the metal complexes, have a deformation bands associated with intermolecular hydrogen bonding were observed at ca.3330 cm⁻¹ to 3100 cm⁻¹ weak. The other characteristics stretching vibrations belonging to C=N and N-O groups were observed at ca. 1464 cm⁻¹ and 1459 cm⁻¹, respectively. The absorptions indicate that the oxime groups participate in complexation. In the metal (II) complexes the coordinated H₂O groups are identified by a broad OH absorption at ca.3300 cm⁻¹ and a wide and low intensity band at ca. 1591 cm⁻¹ and indicates the formation of a

hydrogen bridge reduced the strength of the OH bond. The occurrence of hydrogen bridges by the loss of one oxime proton per oxime molecule during the complexation of these ligands accounts for the two non-identical =N-O- linkage, C=N-O-H in the complexes [10]. The stretching vibrations of the oxime groups appearing at ca. 1464 cm⁻¹ in the free ligands are shifted to ca. 1459 cm⁻¹ in the mononuclear nickel(II), copper(II) and zinc(II) complexes. At the same time, in the complexes the bands observed finger prints near 1070 cm⁻¹ in the free ligand, which is assigned to the N-O, are shifted to lower frequencies (1051 -1045 cm⁻¹) after complexation. New band due to the M-N group of the [ML₂]Cl₂ complexes at the ca. 721 cm⁻¹ appear confirming that nitrogen takes part in the

coordination. The UV-Vis spectra of the metal (II) complexes were taken in DMSO at room temperature. In the UV-Vis spectra of the metal (II) complexes of NiL₂, CuL₂, and ZnL₂ at 282, 268 and 280 and 314 nm, respectively, and at 413, 419, and 439, 668 and 697 nm, respectively, are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively and to charge transfer transition. These all transitions shows bathochromic shift in $n \rightarrow \pi^*$ transition; imply evidencing the participation of these groups in metal ion coordination. However, the d-d transitions could not be recorded for Ni(II)

and Cu(II) complexes due to inadequate solubility.

Under these conditions the binuclear metal(II) complex was prepared by template method. According to reported review [9], firstly, the zinc salt was synthesized with phendione (2) in absolute ethanol. The Zinc-phendione has a metal-ligand ratio of 1:2 according to the elemental analysis. The Zn-phendione complex shows that the phendione coordinated to metal ion through their nitrogen atoms [1-4,10]. Secondly, the zinc-phendioxime was synthesized

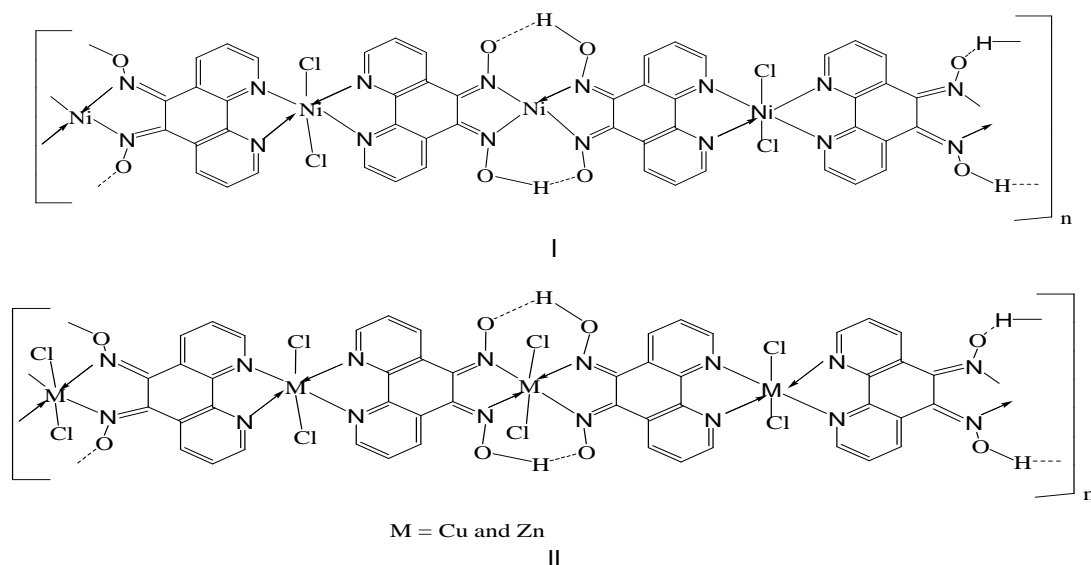
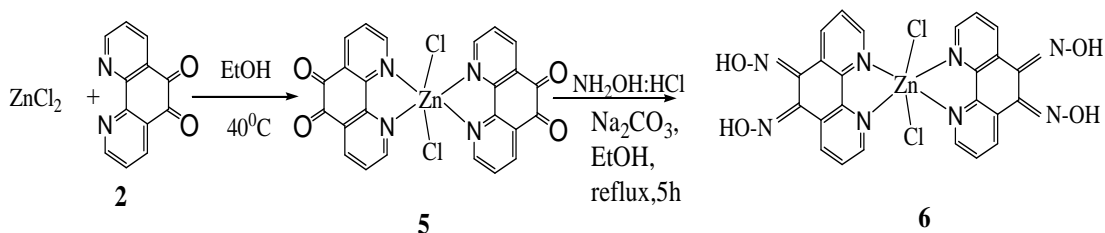


Fig. 2. Suggested structures of square-planar and octahedral complexes of the ligand



Scheme 2. Synthesis of zinc phendioxime complex using template method

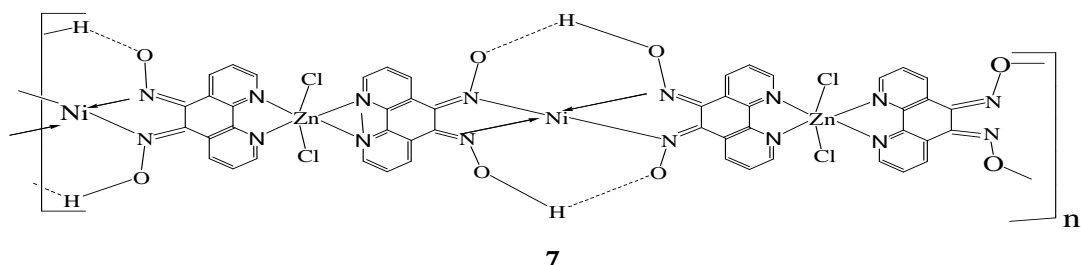


Fig. 3. Suggested formula of the octahedral complex of the ligand

from zinc-phendione with the same procedure of synthesis of phendioxime from phendione. The IR of the binuclear complexes almost similar with the mononuclear complexes. However; the main difference is in spectra at ca. 1045 cm^{-1} , which is very weak, compared to the mononuclear complexes. This indicates the C=N coordinated to two different metal ions which is the phen ring which contain two C=N groups the one coordinated to nickel(II) and the other coordinated to the zinc(II) metal atoms. However; the M-N coordination is the same with mononuclear coordination spectra which is disappear in the free ligand. In UV-Vis. Spectra of the ligands were taken in DMF at room temperature. In the UV-Vis spectrum of N,N'-Zn-PD, a band at 270 nm (37037 cm^{-1}) is assigned to $\pi \rightarrow \pi^*$ transitions. Another band at 406 nm (24631 cm^{-1}) has been assigned to $n \rightarrow \pi^*$ transitions. In the UV-Vis spectrum of N,N'-N,N'-Zn-Ni-PDO a band at 264 nm (37879 cm^{-1}) is assigned to $\pi \rightarrow \pi^*$ transitions and a band at 308 and 350 nm (32467 and 28371 cm^{-1}) have been assigned to $n \rightarrow \pi^*$ transitions. Another band at 668 nm (14970 cm^{-1}) has been assigned to charge transfer transition. The transitions shows bathochromic shift in $n \rightarrow \pi^*$ transition; imply evidencing the participation of this group in metal ion coordination. UV-Vis spectrum of N,N'-Zn-PD and N,N'-Zn-PDO the absorption bands in the UV region are assigned to ligand-centered $\pi \rightarrow \pi^*$ transitions of the N,N' phen. These transitions are at longer wavelengths than the free coordinated precursor and ligand. These imply that one does involve additional conjugation of aromatic ring and non-bonding electrons in the metal orbital. Therefore the intense absorption bands centered at approximately 406 nm and 440 nm are intra ligand transitions. These absorption bands are assigned to $n \rightarrow \pi^*$ of the carbonyl group of PD and dioxime N-OH because these bands are shifted toward longer wavelengths (red shift) in polar aprotic solvents [7]. The spectroscopic data for these complexes may suggests that the PD and ligand coordinated to metal ions from its C=N moieties. UV-Vis spectroscopy shows two intra ligand transition ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$). The presence of the free C=O and N-OH moiety in these complexes have prompted to study the synthesis of polynuclear complexes. UV-Vis spectrum of N,N'-N,N'-Zn-Ni-PDO the absorption bands in the UV region are assigned to complex-centered $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the N,N' phen. These transitions are at shorter wavelengths than the N,N'-Zn-PDO complex. These imply that one does involve additional metal orbital in their

complex. The charge transfer transition at 668 nm is shows to longer wavelength than the N,N'-Zn-PDO complex, imply evidencing the participation of these groups in metal ion coordination.

5. CONCLUSIONS

PDO based metal complexes were successfully synthesized following direct and template methods. For the direct method, firstly, the PDO ligand was successfully synthesized following modified literature procedures. In a second step, different metal salts (Ni, Cu, Zn) were reacted (in a 1:2 metal salt to PDO ligand ratio) to give the M-PDO complexes. All complexes for the three different metals exhibit the same coordination; hexa coordination from phen moiety (four N, N' of the two phen groups and two chlorine atoms) and tetra coordination from oximate moiety (four N,N' of the oximate groups). Via the template method, first PD-Metal was synthesized from a $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ salt and PDO-metal complex prepared from it. Subsequently, a ZnCl_2 was reacted to afford complexes with the same coordination of the direct method but containing two different metals, the first one (Ni) in the tetra coordination site and the second one (Zn) in the hexa coordination site. All ligand and complexes were characterized via ^1H and ^{13}C -NMR, UV-Vis, metal and chloride estimation, elemental analysis, conductivity and magnetic susceptibility analyses. The negligible conductivity of these complexes reveals the coordination of the chloride ion in the inner sphere and non-electrolyte nature of the polynuclear metal complexes. The magnetic susceptibility, the conductance measurement data, the chloride and metal estimation and elemental analysis are also supportive evidences for octahedral geometry of Ni(II) coordinated by N,N' of phen and Cu(II) and Zn(II) complexes coordinated to both N,N' of phen and dioximate groups. Square-planar geometry for Ni-PDO and tetrahedral geometry for Ni in N,N'-N,N'-Zn-Ni-PDO coordinated by N,N' of the dioximate group.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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