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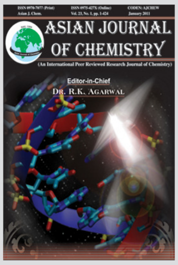

Synthesis and Characterization of Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Glyoxime Hydrazone

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A novel ligand, (1E,2E)-2-(hydroxyimino)-N'-[(1E)-2-oxo-2-phenylethylidene]ethanehydroximohydrazide (LH_2) was prepared by reacting *anti*-glyoxime hydrazine with phenylglyoxal monohydrate in absolute ethanol. On the basis of the magnetic and spectral evidences a square planar geometry for Co(II), Cu(II) and Ni(II) complexes and a tetrahedral geometry for Zn(II) complex are proposed. The ligand and its Co(II), Ni(II), Cu(II) and Zn(II) complexes were determined by elemental analyses, magnetic susceptibility, molar conductance, thermogravimetric analysis (TGA) and spectroscopic (UV-Vis, FT-IR ^1H and ^{13}C NMR) data.

Key Words: *vic*-Dioxime, Glyoxime, Hydrazone, Metal complexes, Extraction.

INTRODUCTION

In recent years, the hydrazones have a widely variety of applications such as hole transporting agents[1] in organic photoconductor layers, in pharmaceutical industry as drugs for treatment of cancer, schizophrenia, leprosy, *etc.*, besides they use in synthetic and industrial chemistry. Furthermore, they have been drawing much attention from coordination chemists, because aryl hydrazones have a strong tendency to chelate transition metals[1,2].

Oximes are used for isolation, purification and characterization as well for protection of carbonyl compounds[3]. Since oximes can be prepared from non-carbonyl compounds, the conversion of oximes into carbonyl compounds provides an alternative method for the preparation of aldehydes and ketones[4]. Some of the methods of generating carbonyl compounds from oximes involve reagents that are often hazardous or very toxic, expensive or not readily available, they need to be freshly prepared or the reactions require drastic conditions, long reaction times and tedious work-up. Thus, a milder, selective, non-hazardous and inexpensive reagent is still in demand[5].

It is well known that *vic*-dioximes and their hydrazone derivatives are capable of forming complexes with different metal ions. Preparation and characterization of complexes of different metal ions with *vic*-dioximes have been reported. Interestingly, 1:2 (metal-ligand ratio) complexes of the oxime and hydrazone derivatives of oxime are also known[6]. The process of solvent extraction is one of the most versatile procedures used for the removal, separation and concentration of metallic species, broadening its applications in the recycling of resources in the field of metallurgy and waste water treatment as demand increases for the development of new approaches to resolve the various problems presented. For this purpose many oxime derivatives have been synthesized and their extraction properties investigated by solvent extraction[7]. Although numerous investigations have been recently reported regarding the extraction of transition metal from aqueous phase into an organic phase by crown ether and calixarene. As yet, reports on solvent extraction with the complexes of oxime compounds are scarce[8,9]. Therefore, we have investigated the solvent extraction of metal cations through oxime compounds. In this work, we have investigated the effectiveness of a novel glyoxime derivative in transferring the transition metals [Ni^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+} and Cr^{2+}] from the aqueous phase into the organic phase.

In this paper, the synthesis and complex formation of a novel substituted glyoximehydrazone of unsymmetrically substituted *vic*-dioximes are reported.

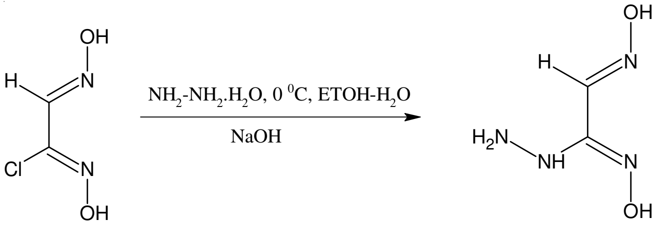
EXPERIMENTAL

Analytical TLC was performed using Merck prepared plates (silica gel 60 F254 on aluminum). All starting materials and reagents used were of standard analytical grade from Fluka, Merck and Aldrich and used without further purification.

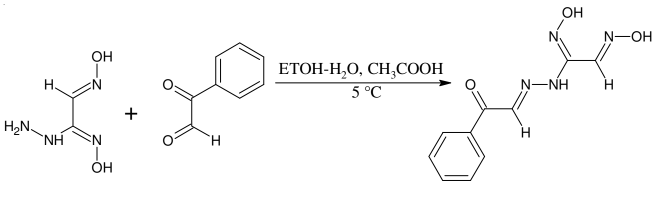
Melting points were determined on a Buchi SPM-20 apparatus in a sealed capillary and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded at room temperature on a Bruker 400 MHz spectrometer in DMSO. IR spectra were obtained on a Varian 900 FT-IR spectrometer using KBr pellets. The absorption spectra were taken on a Shimadzu UV-1601 spectrophotometer. Elemental analyses were obtained using a Leco CHNS-932 analyzer. An Orion Expandable Ion Analyzer EA 940 was used for the pH measurements. The magnetic moments of the complexes were measured by the Gouy method using a Newport type D-104 instrument magnet power supply.

Synthesis: anti-Chloro glyoxime and *anti*-glyoxime hydrazine were prepared according to previously published procedures[10,11].

Synthesis of the ligand (LH_2): A cooled (5 ºC) solution of phenylglyoxal monohydrate (1.76 g, 10 mmol) in absolute ethanol (10 mL) was added dropwise into a cooled solution (5 ºC) containing *anti*-glyoxime hydrazine (1.18 g, 10 mmol) and 3-5 drops CH_3COOH in 10 mL of water with constant stirring. The reaction mixture was stirred for an additonal 4 h at room temperature. The resulting solid compound was filtered off, washed with water and ethanol and dried under reduced pressure. $C_{10}H_{10}N_4O_3$ was obtained in 1.55 g yield (77 %). The reaction steps for the synthesis of LH_2 are given in **Schemes I** and **II**. This compound is soluble in common solvents such as CH_2Cl_2, $CHCl_2$, DMF, EtOH and DMSO. Figs. 1 and 2 show tautomeric forms and intermolecular hydrogen of the ligand (LH_2) bonding, respectively. The observed characteristic ^{13}C NMR peaks of the compound: ($CDCl_3$, TMS, δ ppm): 146.57 (N-NH-C=N-OH), 145.79 (C-CH=N-OH), 151.58 (-CH=N-NH-), 143.51-133.04 (Ar-C). ^1H NMR peaks (DMSO-d_6, ppm): δ 11.80 s, 1H (NH); 11.40-11.50 s, 2H (OH); 8.20-9.30 s, 2H (CH=NOH); 7.48-8.22 m, 5H (Ar-H); 8.45 s, 1H (-CH=N-NH); 8.5 s,1H (O-H).



Scheme-I: Synthesis of *anti*-glyoxime hydrazine (GH_2)[11]



Scheme-II: (1E,2E)-2-(Hydroxyimino)-N'-[(1E)-2-oxo-2-phenylethylidene]ethanehydroximohydrazide (LH_2)

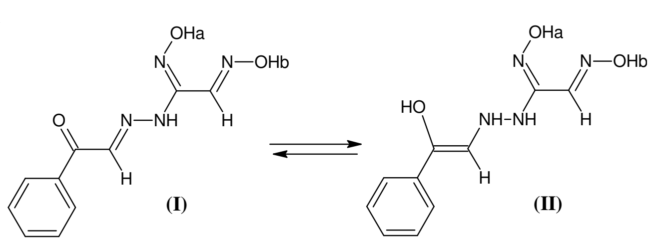


Fig. 1. Tautomeric forms of the ligand (LH_2)

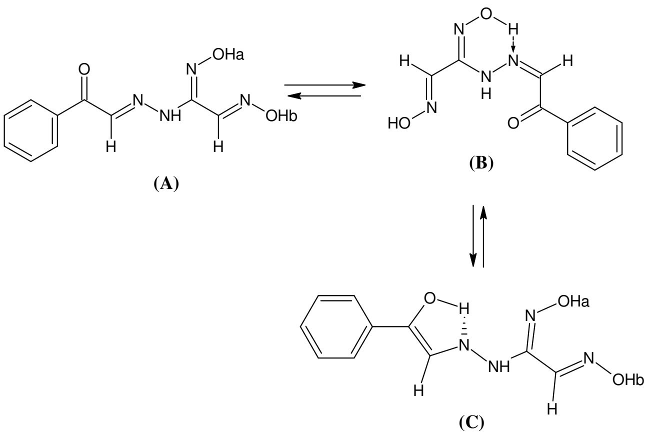
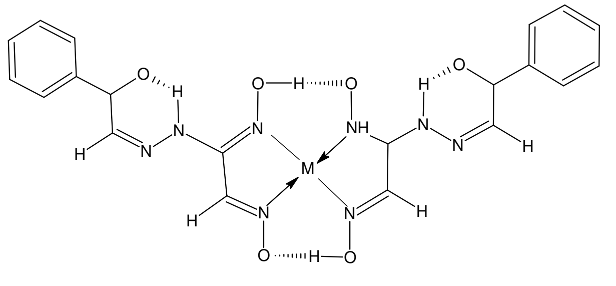
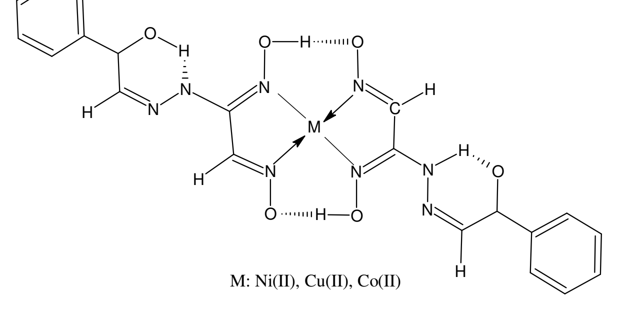


Fig. 2. Intermolecular hydrogen bonding of LH_2

Synthesis of the nickel(II), copper(II) and cobalt(II) complexes: The ligand LH_2 (0.4682 g, 2 mmol) was dissolved in ethanol (15 mL). A solution of the metal salts, [$NiCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol], [$CuCl_2 \cdot 2H_2O$ (0.170 g, 1 mmol)] or [$CoCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol], in water (15 mL) was added dropwise to the ligand solution with continuous stirring at 50 ºC. The stirred mixture was then heated at the reflux temperature for 1 h and was maintained at this temperature. The measured value pH of solutions was *ca.* 3.0-3.5 and was adjusted to 5.0-5.5 by the addition of a 1 % aqueous NaOH solution. The reaction mixture was kept stirring at 60 ºC for 2.5-3.0 h. After cooling to room temperature, the complexes were filtered and washed with water and ethanol several times and dried *in vacuo* at 60 ºC. These compounds were found to be soluble in common organic solvents such as DMSO, DMF, CH_2Cl_2, $CHCl_3$, CCl_4, EtOH, MeOH, acetone, toluene, *n*-hexane, butanol and benzene. Fig. 3 represents a suggested strucutre formulae of square planar complex Ni(II), Cu(II) and Co(II) of the ligand.



a) *cis*-form



M: Ni(II), Cu(II), Co(II)

b) *trans*-form

Fig. 3. A suggested structure formulae of the square planar complex of the ligand

Synthesis of the Zn(II) complex: A solution of $ZnCl_2{\cdot}2H_2O$ (0.172 g, 1 mmol,) in water (20 mL) was mixed with the ligand LH_2 (0.234 g, 1 mmol) dissolved in absolute ethanol (15 mL). The mixture was refluxed on a waterbath at 50 ºC for 1-2 h in order to complete the precipitation. The obtained solid complex was filtered, washed with H_2O and ethanol several times and dried *in vacuo* at 60 ºC. The complex is soluble in common organic solvents such as DMSO, DMF, CH_2Cl_2, $CHCl_3$, CCl_4, EtOH, MeOH, acetone, toluene, *n*-hexane, butanol and benzene. Fig. 4 represents a suggested structure of the complex Zn(II) of the ligand.

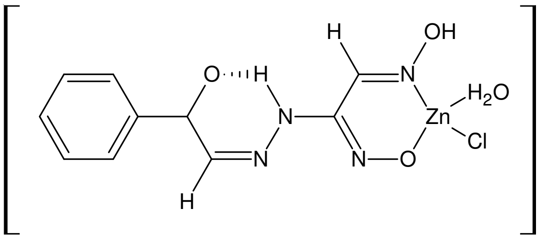


Fig. 4. A suggested structure of the tetrahedral complex of Zn(II)

Solvent extraction: Picrate extraction experiments were performed following Pedersen's procedure[9]. 10 mL of a 2.0×10^{-5} M aqueous picrate solution and 10 mL 1.0×10^{-3} M solution of ligand in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water bath at 25 ºC for 1 h and finally left standing for an additional 0.5 h. The concentration of the picrate ion remaining in the aqueous phase was then determined spectrophotometrically[8]. Blank experiments showed that no picrate extraction occurred in the absence of ligand. The alkali picrates were prepared as described elsewhere[12] by stepwise addition of a 2.0×10^{-2} M aqueous picric acid solution to a 0.14 M aqueous solution of alkali metal hydroxide until neutralization, which was checked by pH control with a glass electrode. They were then rapidly washed with ethanol and ether before being dried *in vacuo* for 24 h. Transition metal picrates were prepared by successive addition of a 1.0×10^{-2} M metal nitrate solution to 2.5×10^{-5} M aqueous picric acid solution and shaken at 25 ºC for 1 h. This metal picrates (Ni^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+} and Cr^{2+}) were measure by UV-Vis using maximum wavelength 352 nm.

RESULTS AND DISCUSSION

As seen from **Schemes-I** and **II**, (1E,2E)-2-(hydroxyimino)-N'-[(1E)-2-oxo-2-phenylethylidene]-ethanehydroximohydrazide (LH_2), was prepared from *anti*-glyoxime hydrazine and phenylglyoxal monohydrate[11].

The resulting compound is soluble in ethanol, pyridine and DMF and DMSO. In general, reactions of the ligand LH_2, with a metal salt were quick and gave a good yield of mononuclear complexes corresponding to the general formula ML_2 and ML. The Ni(II), Cu(II) and Co(II) complexes are proposed to be square planar whereas the complex of Zn(II) is tetrahedral. For the structural characterization of the ligand and its complexes, elemental analyses, FT-IR, UV-Vis, ^1H and ^{13}C NMR spectra, magnetic susceptibility measurements, thermogravimetric analyses were used and the data are given in the experimental section. Additional analytical data are given in Tables 1-4.

Hydrazones synthesized in this work may exit in the keto(I) or in the enol(II) tautomeric form in the solid state (Fig. 1). The observation of strong ν(C= O) absorption bands around 1667-1641 cm^{-1} in the infrared spectra of the ligands suggest that the ligands are in the keto form in the solid state[13,14]. The tautomeric keto forms of compounds were also indicated by ^1H NMR spectroscopy since OH signals of enol forms of ligands were not observed while NH signal of keto forms appeared around 11.80 ppm.

NMR spectra: In the ^1H NMR spectra, since the OH protons of the oxime groups are not equivalent; two peaks for these protons are observed[15,16]. The characteristic oxime OH proton is observed at δ 11.40-11.50 ppm. These chemical shifts are characteristic value for hydrazones and oximes[17,18]. On the basis of ^1H NMR spectra, one can be suggested that LH_2 has the (E,E)- structure. The deuterium-exchangeable protons of =N-OH groups show chemical shifts at δ 8.20 and 9.30 ppm. These singlets also indicate the (E,E)-structure of *vic*-dioximes[19,20]. The other singlet observed at δ 11.80 ppm can be assigned to the NH signal which can also be easily identified by deuterium-exchange (Table-2).

The aromatic protons would resonate as multiples between δ 7.48-8.22 ppm. In the ^1H NMR spectra of LH_2, two absorption bands, which are assigned the oxime OH protons, appear at lower field, at δ 11.40-11.50 and δ 11.80 ppm due to hydrogen bonding. Several isomers which have intermolecular hydrogen bonding can be possible for the synthesized LH_2 in the study (Figs. 1 and 2).

According to FT-IR and ^1H NMR data, isomer B is more suitable owing to the position of strong intermolecular hydrogen bonding (O–H···N). Hence, the peaks appearing at δ 11.40-11.50 ppm and δ 11.80 ppm are attributed to OH proton and NH proton of oxime formulated in Fig. 2, respectively[18].

The chemical shifts belonging to the -OH protons in *vic*-dioxime disappeared in the ^1H-NMR spectrum of the nickel(II) complex and presence of a new resonance at lower field at δ 15.32 ppm were assigned by formation of the hydrogen-bridge which could easily be identified by deuterium exchange[21]. The geometric isomers nickel(II) complex can be inferred from the ^1H NMR spectra, since the alternative chemical environment will show two O—H---O bridge protons in the *cis*-form, but also one ^1H NMR resonance in the *trans*- structure. The observed spectrum has only one ^1H NMR resonance suggesting the *trans*- of the complexes[22]. The structures of both isomers of the complexes are shown in Fig. 3. The mononuclear zinc(II) complex was prepared in 55 % yield by treating $ZnCl_2$ with absolute ethanol. The ligand react with $ZnCl_2$ salt in 1:1 metal:ligand ratios to give complexes two of the four metal coordination sites occupied by the N atom of each oxime group and the O atom of the other group. A chloride ion and a water molecule is also coordinated to the metal ion. In the ^1H NMR spectra zinc(II) complex, the chemical shifts corresponding to the NH proton is observed at frequencies very near to that of the ligand. The ^1H NMR spectrum, shows the presence of coordinated H_2O molecule at δ 3.45 ppm and there is no O···H–O

TABLE-1
ELEMENTAL ANALYTICAL RESULTS AND SOME PROPERTIES OF THE LIGANDS AND COMPLEXES

Compd.	Colour	μ_{eff} (BM)	Λ_M (Ω^{-1} cm^2 mol^{-1})	m.p. (°C)	Yield (%)	Elemental analysis (%): Calcd. (Found)				
						C	H	N	Cl	M
$C_{10}H_{10}N_4O_3$ (LH_2)	Yellow	–	1.3	127	77	51.28 (51.52)	4.30 (4.20)	23.92 (23.28)	–	–
$C_{20}H_{18}N_8O_6Ni$ (**1**)	Dark-Brown	Diamag.	7.4	210	52	45.67 (43.57)	3.43 (3.47)	21.32 (21.28)	–	11.23 (11.51)
$C_{20}H_{18}N_8O_6Cu$ (**2**)	Dark-Green	1.72	6.3	208	73	45.29 (44.94)	3.40 (3.74)	21.14 (20.79)	–	11.98 (12.33)
$C_{20}H_{18}N_8O_6Co$ (**3**)	Dark-Brown	2.87	4.5	227	65	45.67 (43.59)	3.43 (3.39)	21.32 (21.19)	–	11.23 (11.49)
$C_{20}H_{18}N_8O_6Zn$ (**4**)	Yellow	Diamag.	11.7	220	53	45.16 (44.79)	3.39 (3.75)	21.08 (21.45)	20.06 Decomp. (20.17)	12.20 (11.87)

TABLE-2
^{1}H NMR SPECTRA OF THE LIGAND^a AND Ni(II) COMPLEX IN DMSO-d_6 (δ, ppm)

Compound	O–H---O*	O–H^a	N–H^a	CH=NOH	$CH_{Aromatic}$	Other
LH_2	–	11.40-11.50	11.80	8.20-9.30	7.48-8.22	–
$(L^1H)_2Ni$	15.32	–	–	–	–	–
(LH)Zn	N–O···H (9.76)	–	–	–	–	-H_2O (3.45)

*Disappears on D_2O exchange

TABLE-3
CHARACTERISTIC FT-IR BANDS (cm^{-1}) OF THE LIGAND AND COMPLEXES AS KBr PELLETS

Compd.	ν(N-H)	ν(O-H)	ν(C-$H_{arom.}$)	ν(O–H···O)	ν(C=N_{oxime})	ν(C=$N_{hyd.}$)	ν(N-O)	ν(C =O)
LH_2	3420	3230	3055	1740	1610	1540	1005	1670
1	3245	3190	3055	2170	1545	1590	980	–
2	3440	3340	3065	2340	1540	1595	990	–
3	3350	3240	3060	2360	1545	1595	970	–
4	3378	3430	3005	1780	1625	1606	950	–

TABLE-4
CHARACTERISTIC UV-VIS BANDS OF
THE LIGAND AND COMPLEXES

Compounds	Solvent	Wave length, λ_{max} (nm)
LH_2	ETOH	345, 295
1	DMSO	678, 546, 488, 350
2	DMSO	637, 450, 325, 280
3	DMSO	648,420, 350, 300
4	DMSO	410, 364, 297, 280

peaks as expected for complex formulae in Fig. 4, but there is resonance at δ 9.76 ppm, which is assigned to N–OH[21].

A ^{13}C NMR spectrum is one of the most convenient ways to prove the true structure of *vic*-dioxime. In the ^{13}C NMR spectrum of LH_2, the carbon resonances of the oxime groups, are observed at 146.57 and 145.79 ppm. Observation of *vic*-dioxime and -OH protons in the ^{1}H NMR and of dioxime carbons in the ^{13}C NMR spectra at two different frequencies in each case, indicates that the *vic*-dioxime has an *anti*-structure[23]. The equivalent carbon atoms, especially the adjament hydroxyimino groups, also confirm the (E,E)-structure of *vic*-dioximes[24].

FT-IR spectra: The tentative assignments of the most characteristic IR bands were observed and are given in Table-3. The FT-IR. spectrum of the -OH group of oxime shows stretching vibration at 3450 and 2600 cm^{-1} instead of a band at *ca.* 3230 cm^{-1} because of an intermolecular hydrogen bonding N···H–O–[25].

Also the NH stretching band of LH_2 was not observed in the FT-IR spectra probably due to overlapping with the intermolecular hydrogen-bonded O-H stretching frequency. The stretching band of the imine group C=N of these compounds was observed at 1611 cm^{-1}. The stretching belonging to the -NH and N-O groups occur at 1005 and 3420 cm^{-1}, respectively. These values are in agreement with the previously reported hydrazone and oxime derivatives[17,18].

The FT-IR spectra of the Ni(II), Cu(II) and Co(II) have been compared with those for similar compounds in order to establish the coordination modes of the oxime ligands in these complexes[11,21]. The more relevant OH, C=N and N-O absorption bands are given in Table-3. The Ni(II), Cu(II) and Co(II) complexes have FT-IR spectra very similar to those of the free ligand, except for he absence of the O-H stretching vibrations. A weak and low intensity band at 2360-1780 cm^{-1} indicates the formation of the hydrogen bridge during complexation of the ligand, since the hydrogen bridge reduces the strength of the O-H bond. The occurrence of hydrogen bridges by the loss of one oxime proton per oxime molecule during the complexation of this ligand accounts for the two non-identical =N-C- linkages, C=N-O-H in the complexes[26]. The stretching vibrations of the azomethine groups appearing at 1611 cm^{-1} in the free ligand is shifted to 1625-1540 cm^{-1} in the mononuclear Ni(II), Cu(II) and Co(II) complexes. At the same time, in the complexes the bands observed near 1005 cm^{-1} in the free ligand, which are assigned to the ν(N-O) are shifted to lower frequencies (950-990 cm^{-1}) after complexation.

In the FT-IR spectrum of the zinc(II) complex, coordinated H_2O molecule is also identified by a broad OH absorption at *ca.* 3430 cm^{-1}. The stretching bands of C=N and N-O appearing at 1610 and 1005 cm^{-1} in ligand is shifted to 1625 and 950 cm^{-1} for zinc(II) complexes. There is no O···H–O peak as expected for complex formulae[21].

Electronic spectra: The electronic spectrum of the ligand and its complexes were recorded in ethanol and DMSO (Table-4). In the electronic spectra of the ligand and its metal complexes, the 230-385 nm band seems to be due to both the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions of C=N and charge-transfer transition arising from p electron interactions between the metal and ligand which involves either a metal-to-ligand or ligand-to-metal electron transfer[27].

The electronic spectra of the nickel(II), cobalt(II) and copper(II) complexes show absorption bands at 678, 637 and 648 nm attributed to the $^1A_{1g} \rightarrow {}^1B_{1g}$ for nickel(II) and Co(II) complexes and $^2T_{2g} \rightarrow {}^2E_g$ for copper(II) complex transitions, which are compatible with the complexes having a square planar structure[28]. The electronic spectrum of the zinc(II) complex shows an absorption band at 410 nm which is attributed to the L-M (charge-transfer) transition, compatible with a tetrahedral structure[21].

Magnetic susceptibility: The structures of the mononuclear complexes are supported by magnetic moment data. The nickel(II) and zinc(II) complex are diamagnetic as expected for d^8 and d^{10} electronic configurations[29]. The cobalt(II) and copper(II) complexes are paramagnetic and their magnetic moments are 2.87 and 1.72 BM, respectively. The alternative chemical environments will give two (O···H–O) bridge protons in the *cis*-form, but only one in the *trans*-form. Observation of the (O···H–O) in the IR spectrum and ^{1}H NMR spectra, at one frequency in each case, indicate that the nickel(II) complex is in the anti-form media. According to the above results, square-planar geometry for the nickel(II) and copper(II) and cobalt(II) complexes and tetrahedral geometry for the zinc(II) complex are proposed[11, 21,23].

Molar conductance: As seen from the Table-1, the molar conductance measured in DMSO solution (*ca.* 1×10^{-3} M) for the ligand and its mononuclear complexes is in the range of 1.3-11.7 Ω^{-1} cm^2 mol^{-1}. This result shows that the complexes are non-electrolytes[21].

Thermal study: The thermogravimetric curves were obtained at a heating rate of 10 ºC/min in a N_2 atmosphere over 25-800 ºC range. The ligand (LH_2) is stable up to 120 ºC, but then decomposes in two steps corresponding to the 120-370 and 370-650 ºC ranges. In the TGA curve of the Zn(II) complex, 3.95 % weight loss was observed at 167 ºC for [Zn(LH)(Cl)(H_2O)]. This shows that the zinc(II) complexes contain one coordinated water molecule. In addition, the thermal stability of all complexes increases in the order: Ni < Cu < Co < Zn. When the complexes are heated to the higher temperatures, they decompose to give oxides of the MO type[30,31].

Solvent extraction: Up to now, studies related with solvent extraction with complexes of oxime compounds are very limited. Therefore, this work focused on elaboration of strategic requirements for the two-phase extraction measurements. Solvent extraction is one of the most versatile procedures among the separation techniques used for the removal, separation and concentration of metals. For this purpose many oxime derivatives have been synthesized and their extraction properties have been investigated by solvent extraction. In this work the binding efficiencies of synthesized *vic*-dioxime derivatives insoluble in major organic solvents and immiscible with aqueous phase were evaluated by solid-liquid extraction under neutral conditions. The results are listed in Table-5.

TABLE-5
EXTRACTION OF METAL PICRATES WITH LIGAND

Ligand	Picrate salt extracted (%)						
	Ni^{2+}	Cu^{2+}	Co^{2+}	Cd^{2+}	Zn^{2+}	Mn^{2+}	Cr^{2+}
LH_2	68.6	83.1	53.8	64.5	76.4	54.7	48.5

Aqueous phase, [metal nitrate] = 1×10^{-2} M;
Solid phase [LH_2, (234×10^{-3} g)] at 25 ºC for 4 h.

The effectiveness in transferring transition metals rather than the other metal cations by the synthesized compounds indicates that a cation-*p* electron interaction is operative since the metal is bounded by the opposite N, N or N, O sites of these compounds[9,32,33].

The compound LH_2 showed the highest extractability toward Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} cations. Copper(II) was the most efficiently extracted metal ion. The metals were bound by the opposite N, N or N, O sites of these compounds. Moreover, the carbonyl group of hydrazone side of such compounds, which is an electron donor group, may interact with the metal ions. The presence of soft donor C=N-OH and C=O groups in the ligands, which show high affinity to transition metals, resulted in the increase of the extraction ability of these compounds[32].

The cations studied were some transition metals Ni^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+} and Cr^{2+}. The results are summarized in Table-5.

Conclusion

In this study, a novel ligand, (1E,2E)-2-(hydroxyimino)-N'-[(1E)-2-oxo-2-phenyl ethylidene]ethanehydroximohydrazide (LH_2) and its mononuclear Co(II), Cu(II), Ni(II) and Zn(II) complexes were synthesized and characterized by elemental analysis, magnetic susceptibility measurements, FT-IR and ^{13}C NMR and ^{1}H NMR. Elemental analysis, stoichiometric and spectroscopic data of the metal complexes indicated that mononuclear complexes of LH_2 has a metal to ligand mole ratio of 1:2. However, the reaction of the ligand with salt of Zn(II) gave products with metal:ligand ratio of 1:1 (Figs. 3 and 4). According to the magnetic susceptibility results, all complexes of the oxime ligand have square planar or tetrahedral geometry.

Furthermore, the cation-binding properties of the novel ligand (LH_2) for Ni^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+} and Cr^{2+} picrates were investigated in a CH_2Cl_2/H_2O system at 25 ºC. The compound LH_2 showed the highest extractability toward Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} cations. Copper(II) was the most efficiently extracted metal ion. The metals were bound by the opposite N, N or N, O sites of these compounds. Moreover, the carbonyl group in the hydrazone side of such compounds, which is an electron donor group, may interact with the metal ions. Recovery of valuable metal pollutants from air and water is very important and the prepared compound can be used for this purpose.

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