

Synthesis of *vic*-Dioxime Derivatives with Hydrazone Side Groups and Their Metal Complexes

İlknur BABAHAN^{1*}, Hüseyin ANIL², Nursabah SARIKAVAKLI¹

¹Department of Chemistry, Adnan Menderes University, 09010, Aydın-TURKEY

²Department of Chemistry, Ege University, 35040, Bornova, İzmir-TURKEY

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Two novel *vic*-dioxime (L^1H_2 , L^2H_2) compounds bearing hydrazone side groups and their transition metal complexes Ni(II), Co(II), Cu(II), and Zn(II) were synthesized. The *vic*-dioxime ligands bearing hydrazone side groups were synthesized by reacting *anti*-glyoximehydrazine (GH_2) with 4-nitroacetophenone and 4-methylacetophenone, respectively. Ligands form mononuclear complexes $[(LH)_2M]$ with a metal to ligand ratio of 1:2 with $M=Co(II)(H_2O)_2$, Ni(II), and Cu(II). Zn(II) forms complexes $[(LH)(H_2O)(Cl)Zn]$ with a metal to ligand ratio of 1:1. The Co(II) complexes of the ligands are proposed to be octahedral with water molecules as axial ligands, the Ni(II) and Cu(II) complexes are proposed to be square planar, and the complexes of Zn(II) are tetrahedral. A chloride ion and a water molecule are also coordinated to the Zn(II) ion. Structural assignments are supported by a combination of ¹H-NMR, ¹³C-NMR, HMQC, FT-IR, elemental analyses, and magnetic susceptibility.

Key Words: *vic*-Dioximes, hydrazone compounds, transition metal complexes.

Introduction

Recently, since the increasing use of coordination compounds in analytical, bio, pigment, and medicinal chemistry, many investigators have studied these topics, especially the important roles of the complexes of 1,2-dioximes in coordination chemistry. Studies of the complexes began by investigations of the reaction of dimethylglyoxime with Ni(II) by Tschugaeff in 1905¹.

vic-Dioxime complexes are an important group of coordination compounds from different aspects. These classes of compounds are employed as the model compounds for examining the structure of vitamin B₁₂ and coenzyme B₁₃, which have important roles in biological mechanisms. Additionally, they are also important in medical, chromatographic, and analytical applications².

Intensified interest in the complexes of transition metals with hydrazides and hydrazones developed as a consequence of their increasing application in medicine, analytical chemistry, syntheses of novel heterogeneous catalysts of oxido-reduction processes, as well as in numerous fields of science and technology.

*Corresponding author

Among ligand systems, hydrazones are special because, quite a number of these compounds express biological activity and complex formation with transition metals, sometimes resulting in a several-fold increase in this activity. This enables their application as antitumor, antiviral, bactericide, and psychotropic agents³.

The chemical properties of hydrazones have been intensively investigated in several research areas because of their chelating capability and their pharmacological applications. The antibacterial and antifungal properties of bis acylhydrazone and their complexes with some first transition metal ions were studied and reported by Carcelli et al.⁴. They noted good activity against Gram-positive bacteria in vitro for some of the complexes⁴.

Many studies of hydrazones, and mono- and dioximes have been carried out; yet, little information related to the derivatives of *vic*-dioximes with hydrazone side groups was found in the literature⁵. Herein, the novel *anti*-4-nitroacetophenoneglyoxime hydrazone (L^1H_2) and *anti*-4-methylacetophenoneglyoxime hydrazone (L^2H_2), and their complexes with Ni(II), Cu(II), Co(II), and Zn(II) ions are described.

Experimental

Materials and Instrumentation

All reagents used were purchased from Merck and used as received. Elemental analyses, ¹H-NMR and ¹³C-NMR spectra (Bruker 400 MHz), IR spectra (Varian 900), melting points (Buchi SPM-20), and pH measurements (Orion Expandable Ion Analyzer EA 940) were used to elucidate the structures of the products. The magnetic moments of the complexes were measured by the Gouy method with a Newport type D-104 magnet power supply.

Preparation of the Ligands

anti-Chloroglyoxime was prepared according to previously published procedures⁶.

Synthesis of L^1H_2 and L^2H_2

L^1H_2 and L^2H_2 were synthesized from the starting materials, namely *anti*-glyoximehydrazine (GH_2)⁵ (Scheme 1), 4-nitroacetophenone (for L^1H_2), and 4-methylacetophenone (for L^2H_2), using glacial acetic acid as a catalyst. A cooled (5 °C) solution of ketone (1 mmol) in ethanol was added dropwise into a cooled solution (5 °C) containing (1 mmol) GH_2 ⁵ and 3-5 drops of CH_3COOH with constant stirring. After the addition of the ketone solution was completed, the solution was stirred for an additional 4-8 h at room temperature. The resulting solid compounds were filtered off, washed with water and ethanol, and dried in a vacuum oven. The chemical reaction and molecular structure are shown in Scheme 2. Results of the compositional and spectroscopic analyses are shown in Tables 1-3.

Synthesis of the Ni(II), Co(II), Cu(II) Complexes of Ligands

A solution of a metal salt (1 mmol of $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ or $CuAc_2 \cdot H_2O$) in 20 mL of water was added to 2 mmol of the L^1H_2 and L^2H_2 ligand solution (0.530 g (2 mmol) L^1H_2 in 15 mL of ethanol, 0.468 g (2 mmol) L^2H_2 in 15 mL of ethanol) with stirring. An initial sharp decrease in the pH of the solution from 5.5 to about 3-3.5 was observed. After raising the pH to 5-5.5 using a 1% aqueous NaOH solution, the reaction

mixture was kept in a hot water bath (60 °C) for 2 h to complete the precipitation. Then the precipitated complex compounds were filtered, washed with water, and dried at room temperature in a vacuum oven. The complexes are very slightly soluble in common organic solvents. Results of the compositional and spectroscopic analyses are shown in Tables 1 and 2. The structures of the complexes are shown in Figure 1.

Synthesis of the Zn(II) Complexes of Ligands

A solution of ZnCl₂·2H₂O (0.172 g, 1 mmol) in ethanol (20 mL) was added to a solution of ligand (0.265 g (1 mmol) for L¹H₂ and 0.234 g (1 mmol) for L²H₂), dissolved in ethanol (20 mL) by stirring in a water bath at 50 °C for 2 h in order to complete precipitation. The apparent pH of the solution was adjusted to 5.0-5.5 by the addition of 1 M NaOH solution. The precipitate was filtered, washed with water, and dried in vacuo at 60 °C. The complexes are very slightly soluble in common organic solvents. Results of the compositional and spectroscopic analyses are shown in Tables 1 and 2. The structures of the complexes are shown in Figure 2.

Table 1. Color, melting points, yields, and elemental analytical results of the ligands.

Compounds	Formulas (MW)	Color	M.p. ^a (°C)	Yield (%)	Calculated (Found) %		
					C	H	N
L ¹ H ₂	C ₁₀ H ₁₁ O ₄ N ₅ (265.226 g.mol ⁻¹)	Yellow	157	70	45.28 (45.50)	4.18 (4.72)	26.41 (26.12)
[Ni(L ¹ H) ₂]	C ₂₀ H ₂₀ O ₈ N ₁₀ Ni (587.129 g.mol ⁻¹)	Red	249 ^a	68	40.91 (40.36)	3.43 (3.87)	23.86 (23.56)
[Co(L ¹ H) ₂ (H ₂ O) ₂]	C ₂₀ H ₂₄ O ₁₀ N ₁₀ Co (623.399 g.mol ⁻¹)	Brown	> 400	55	38.53 (39.18)	3.88 (3.76)	22.47 (21.74)
[Cu(L ¹ H) ₂]	C ₂₀ H ₂₀ O ₈ N ₁₀ Cu (591.981 g.mol ⁻¹)	Brown	> 400	60	40.58 (41.34)	3.41 (3.38)	23.66 (23.05)
[Zn(L ¹ H)(Cl)(H ₂ O)]	C ₁₀ H ₁₂ O ₅ N ₅ ClZn (383.076 g.mol ⁻¹)	Red	> 400	72	31.35 (31.65)	3.16 (2.41)	18.28 (18.28)
L ² H ₂	C ₁₁ H ₁₄ O ₂ N ₄ (234.255 g.mol ⁻¹)	Yellow	149	75	56.40 (56.64)	6.02 (5.23)	23.92 (23.80)
[Ni(L ² H) ₂]	C ₂₂ H ₂₆ O ₄ N ₈ Ni (525.187 g.mol ⁻¹)	Red	254 ^a	80	50.31 (50.18)	4.99 (4.53)	21.34 (21.83)
[Co(L ² H) ₂ (H ₂ O) ₂]	C ₂₂ H ₃₀ O ₆ N ₈ Co (561.457 g.mol ⁻¹)	Brown	> 400	56	47.06 (47.72)	5.39 (4.87)	19.96 (19.29)
[Cu(L ² H) ₂]	C ₂₂ H ₂₆ O ₄ N ₈ Cu (530.039 g.mol ⁻¹)	Brown	182 ^a	65	49.85 (49.41)	4.94 (4.56)	21.14 (21.70)
[Zn(L ² H)(Cl)(H ₂ O)]	C ₁₁ H ₁₅ O ₃ N ₄ ClZn (352.105 g.mol ⁻¹)	Yellow	> 400	52	37.52 (38.27)	4.29 (3.51)	15.91 (16.36)

^awith decomposition

Results and Discussion

In this work, 2 novel *vic*-dioxime (L¹H₂, L²H₂) compounds bearing hydrazone side groups and their transition metal complexes Ni(II), Co(II), Cu(II), and Zn(II) were synthesized. The *vic*-dioxime ligands bearing hydrazone side groups were synthesized by reacting *anti*-glyoximehydrazine (GH₂)⁵ with 4-nitroacetophenone and 4-methylacetophenone, respectively. Novel ligands were characterized by a combination of ¹H-NMR, ¹³C-NMR, HMQC, FT-IR, and elemental analytical techniques. The structures of the complexes were

Table 2. Magnetic moments and characteristic IR bands^a of the ligands and their metal complexes as KBr pellets cm⁻¹.

Compounds	Mag. Mom. (per metal) ^a B.M	$\nu(\text{NH})$	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$ oxime	$\nu(\text{C}=\text{N})$ hydrazone	$\nu(\text{C}-\text{H})$ aromatic	$\nu(\text{C}-\text{H})$ aliphatic	$\nu(\text{N}-\text{O})$	$\nu(\text{OH}-\text{O})$
L ¹ H ₂	-	3400 (b)	3317 (b)	1617 (s)	1653 (m)	3023 (w)	2917 (w)	900 (s)	-
[Ni(L ¹ H) ₂]	diamagnetic	3361 (b)	-	1607 (s)	1633 (m)	3039 (w)	2921 (w)	942 (s)	2219 (w)
[Co(L ¹ H) ₂ (H ₂ O) ₂]	4.30	3019 (b)	3370 (b)	1611 (s)	1621 (m)	3067 (w)	2908 (w)	944 (s)	2219 (w)
[Cu(L ¹ H) ₂]	1.74	3350 (b)	-	1604 (s)	1646 (m)	3042 (w)	2915 (w)	943 (s)	2217 (w)
[Zn(L ¹ H)(Cl)(H ₂ O)]	diamagnetic	3369 (b)	3400 (b)	1594 (s)	1624 (m)	3074 (w)	2928 (w)	942 (s)	-
L ² H ₂	-	3366 (b)	3259 (b)	1605 (s)	1651 (m)	3021 (w)	2929 (w)	920 (s)	-
[Ni(L ² H) ₂]	diamagnetic	3354 (b)	-	1559 (s)	1621 (m)	3017 (w)	2914 (w)	942 (s)	2316 (w)
[Co(L ² H) ₂ (H ₂ O) ₂]	4.31	3321 (b)	3392 (b)	1561 (s)	1615 (m)	3017 (w)	2922 (w)	950 (s)	2366 (w)
[Cu(L ² H) ₂]	1.25	3353 (b)	-	1558 (s)	1621 (m)	3010 (w)	2914 (w)	932 (s)	2312 (w)
[Zn(L ² H)(Cl)(H ₂ O)]	diamagnetic	3263 (b)	3367 (b)	1556 (s)	1627 (m)	3030 (w)	2919 (w)	936 (s)	-

^aby using molar susceptibility.

b = broad, s = strong, m = medium, w = weak.

characterized by FT-IR, elemental analysis, and magnetic measurements. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of these complexes could not be taken because of their very low solubility in organic solvents⁷. Some physical properties, elemental, analytical, and magnetic susceptibility data of the ligands and complexes are given in Table 1. FT-IR data of the ligands and their complexes are given in Table 2. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ data of the ligands are given in Table 3.

Table 3. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the ligands^{a,b} in DMSO-d_6 in δ (ppm).

$^1\text{H-NMR}$ spectra of the ligands		
Groups	L^1H_2	L^2H_2
-OH ^c	11.55 (s, 1H)	11.48 (s, 1H)
	10.84 (s, 1H)	10.63 (s, 1H)
-NH ^c	8.95 (s, 1H)	8.59 (s, 1H)
$\text{CH}=\text{NOH}$	7.98 (s, 1H)	7.96 (s, 1H)
Ar-H	8.21 (d, 2H, J=8.65)	7.59 (d, 2H, J=8.88)
	7.93 (d, 2H, J=8.65)	7.17 (d, 2H, J=8.88)
-CH ₃	2.26 (s, 3H)	2.32 (s, 3H) 2.19 (s, 3H)
$^{13}\text{C-NMR}$ spectra of the ligands		
$\text{HNC}=\text{NOH}$	146.16	146.05
$\text{HC}=\text{NOH}$	141.64	141.87
$\text{MeC}=\text{NNH}$	147.63	146.56
Ar-C	145.12-143.74-127.28-124.28	138.69-136.14-129.62-126.27
-CH ₃	12.78	21.46-12.83

^aChemical shifts(δ) are reported in ppm relative to SiMe_4 at 30 °C, s: singlet, d: doublet, ^bin DMSO-d_6

^cDisappears on D_2O exchange.

In the IR spectrum of the new hydrazone-oxime compounds, an O-H stretching vibration was observed at 3317 cm^{-1} for L^1H_2 and at 3259 cm^{-1} for L^2H_2 as a broad absorption^{5,8}. The characteristic bands of hydrazone C=N are 1653 cm^{-1} for L^1H_2 and 1651 cm^{-1} for L^2H_2 ^{5,9}. The other characteristic bands of oxime C=N are 1617 cm^{-1} L^1H_2 and 1605 cm^{-1} L^2H_2 ^{10,11}.

N-H and N-O stretching vibration bands of the ligands were shown at 3400 and 900 for L^1H_2 , and 3366 and 920 for L^2H_2 . These values are in accord with the previously reported oxime derivatives^{5,10,11}. Furthermore, CH stretching vibrations were shown between 2917 and 2824 cm^{-1} for L^1H_2 , and between 2929 and 2848 cm^{-1} for L^2H_2 ¹¹⁻¹³.

Ligands form mononuclear complexes $[(\text{LH})_2\text{M}]$ with a metal to ligand ratio of 1:2 with $\text{M}=\text{Co(II)(H}_2\text{O)}_2$, Ni(II) , and Cu(II) . Zn(II) forms complexes $[(\text{LH})(\text{H}_2\text{O})(\text{Cl})\text{Zn}]$ with a metal to ligand ratio of 1:1^{10,14,15}. The Co(II) complexes of the ligands are proposed to be octahedral with water molecules as axial ligands, while the Ni(II) and Cu(II) complexes are proposed to be square planar, and the complexes of Zn(II) are tetrahedral. A chloride ion and a water molecule are also coordinated to the Zn(II) ion. The Zn(II) complexes are tetrahedral with a 1:1 metal to ligand ratio, according to the elemental analyses, and the ligand is coordinated only by the N, O atoms of the *vic*-dioxime^{10,14,15}.

In the IR spectrum of Co(II) complexes, the weak deformation vibration band assigned to the intramolecular hydrogen bond O-H...O bending vibration is observed around $2366-2219\text{ cm}^{-1}$ ^{5,12,15}. The C=N stretch decreases from $1617-1605\text{ cm}^{-1}$ in the free ligands to $1611-1561\text{ cm}^{-1}$ in Co(II) complexes^{5,10-12,14,15}. For

$[(L^1H)_2Co(H_2O)_2]$ and $[(L^2H)_2Co(H_2O)_2]$, coordinated H_2O molecules are identified by a broad OH absorption around $3392-3370\text{ cm}^{-1}$, with constant intensities after heating above $110\text{ }^\circ\text{C}$ for 24 h. The IR spectra of Ni(II) and Cu(II) complexes exhibit a C=N stretching vibration around $1607-1558\text{ cm}^{-1}$. This vibration is at a lower frequency than for the free ligands, which is attributable to N,N-chelation^{5,10-15}. A weak band around $2316-2217\text{ cm}^{-1}$ can be assigned to the intramolecular hydrogen bond O-H...O bending vibration^{5,12,15}. The intensity of characteristic stretching and bending vibrations of the free ligands were shifted and lowered on complex formation, and new vibrational bands characteristic of the Ni(II) and Cu(II) complexes were observed.

The stretching band of C=N at $1617-1605\text{ cm}^{-1}$ in ligands is shifted to $1594-1556\text{ cm}^{-1}$ for Zn(II) complexes. This suggests that the ligand is coordinated through nitrogen and oxygen donors^{10,14,15}. A chloride ion and a water molecule are also coordinated to Zn(II). A broad band around $3400-3367\text{ cm}^{-1}$ was observed in the spectra of the complexes, due to the coordinated water. There is no O-H...O peak as expected for complexes of formulae shown in Figure 2^{10,14,15,16}.

It is known that Ni(II), Co(II), and Cu(II) metal complexes of dimethylglyoxime are 5-membered chelate structures and the metal ion coordinates to the nitrogen atoms of the dioxime groups. A hydrogen atom separates each of the 2 oxime groups, and as a result a hydrogen bridge is established⁵.

The band (O-H...O) is absent in the FT-IR spectra of the ligands, but appears in FT-IR spectra of the complexes, showing that the complexes of the ligands Ni(II) and Cu(II) have square-planar structures^{1,5} (Figure 1). The red color of Ni(II) complexes of the ligands indicates that the ligands are in the (*E, E*) form, the *anti*-form of the ligands¹⁰.

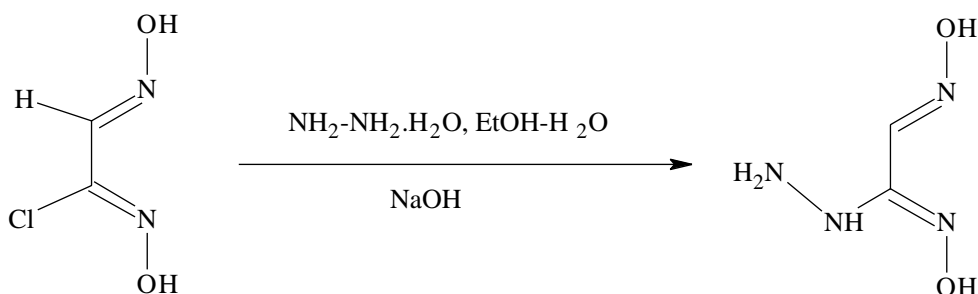
The tetrahedral structure of the Zn(II) complex is based on the disappearance of the band (O-H...O) of the complexes and appearance of the O-H bands of these compounds in the FT-IR spectra^{14,16} (Figure 2).

When the ¹H-NMR spectra of the ligands in DMSO were examined, peaks corresponding to N-OH protons (11.55 ppm and 10.84 ppm (s, 2H) for L^1H_2 , and 11.48 ppm and 10.63 ppm (s, 2H) for L^2H_2) were observed downfield^{5,11,12,17}. The peaks of the NH proton of ligands appear at 8.95 ppm (s, 1H) for L^1H_2 and 8.59 ppm (s, 1H) for L^2H_2 ^{5,17,18}. The vanishing of these peaks by the addition of D_2O to the ligand solution indicates that the observed resonances are those of the protons of O-H and N-H groups. These values are in accord with the previously reported oxime derivatives^{11,17-19}.

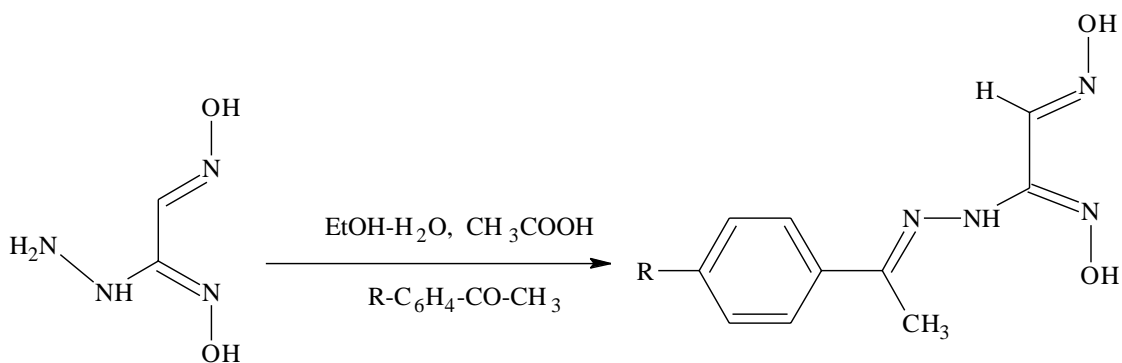
C-H protons next to oxime groups were observed at 7.98 ppm (s, 1H) for L^1H_2 and 7.96 ppm (s, 1H) for L^2H_2 ^{5,11,18,20,21}. The signals of CH_3 appear at 2.26 ppm (s, 3H) for L^1H_2 and 2.32-2.19 ppm (s, 6H) for L^1H_2 ^{11,12}. In the ¹H-NMR spectra, 2 peaks are present for the O-H protons of the oxime groups. These 2 deuterium-exchangeable singlets correspond to 2 non-equivalent O-H protons that also indicate the *anti*-configuration of the O-H groups relative to each other^{11,17,18}. As expected, the aromatic protons of compounds appear at 8.21 (d, 2H)-7.93 (d, 2H) ppm for L^1H_2 and 7.59 (d, 2H)-7.17 (d, 2H) ppm for L^2H_2 , as 2 different doublets^{12,13}.

In the ¹³C-NMR spectrum of ligands, different signals, which were observed at 146.16 ppm for L^1H_2 , 146.05 ppm for L^2H_2 ($HNC=N-OH$), 141.64 ppm for L^1H_2 , and 141.87 ppm for L^1H_2 ($H-C=N-OH$), show asymmetrically substituted *vic*-dioximes^{14,20,21}. ¹³C-NMR spectra at 2 different frequencies in each case indicates that the *vic*-dioxime has the *anti*-structure^{22,23}. Spectra of ($MeC=N-N$) appear at 147.63 ppm

for L^1H_2 and 146.56 ppm for L^2H_2 , as expected²². The signals of the $C_{aromatic}$ carbon were observed at 145.12-143.74-127.28-124.28 ppm for L^1H_2 and 138.69-136.14-129.62-126.27 ppm for L^2H_2 , as 4 peaks^{21,22}. The signals of CH_3 were shown at 12.78 ppm for L^1H_2 and 21.46-12.83 ppm for L^2H_2 ²⁰.



Scheme 1. Synthesis of *anti*-glyoximehydrazine (GH_2)⁵



Scheme 2. Synthesis of ligands (R= nitro for L^1H_2 , methyl for L^2H_2)

The magnetic susceptibility measurements of the Ni(II) and Zn(II) complexes indicate that these complexes are diamagnetic and the magnetic moments of the Cu(II) and Co(II) complexes are 1.74-1.25 and 4.30-4.31 B.M. (Table 1), respectively. These results indicate an octahedral geometry for the Co(II) complexes^{10,14,23}. These results are in good agreement with the square-planar structures of the Cu(II) complexes^{5,7}.

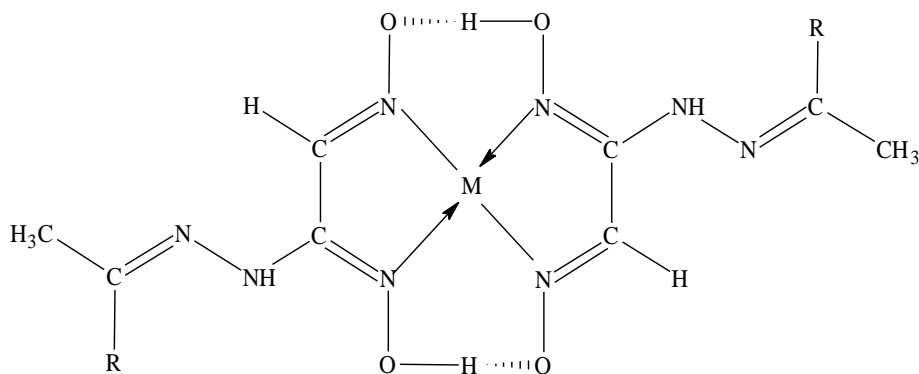


Figure 1. Suggested structure of the Co(II)-2H₂O, Ni(II), and Cu(II) complexes (R= 4-nitrophenyl, 4-methylphenyl).

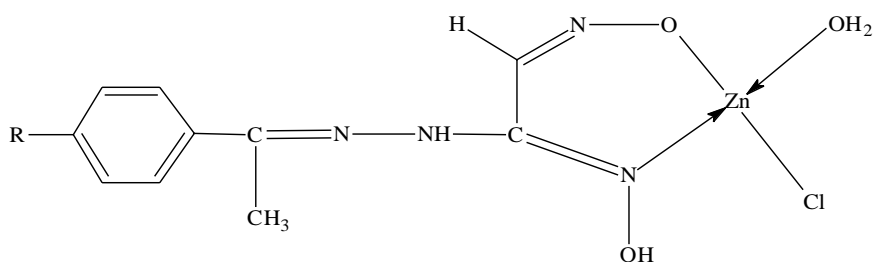


Figure 2. Suggested structure of Zn(II) complexes (R= nitro, methyl).

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