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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

A Novel Reaction of α-Carbonyl Oxime and Amido Alcohol: Synthesis, Characterization, Crystal Structure, and Thermal Studies of an Amido Alcohol, a New Oximino Alcohol Ligand, and its Metal Complexes

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Published online: 11 Aug 2011.

To cite this article: Yunus Kaya, Gazi Irez, Hasene Mutlu & Orhan Buyukgungor (2011) A Novel Reaction of α-Carbonyl Oxime and Amido Alcohol: Synthesis, Characterization, Crystal Structure, and Thermal Studies of an Amido Alcohol, a New Oximino Alcohol Ligand, and its Metal Complexes, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 41:7, 754-762, DOI: 10.1080/15533174.2011.591300

To link to this article: http://dx.doi.org/10.1080/15533174.2011.591300

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ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2011.591300

A Novel Reaction of α-Carbonyl Oxime and Amido Alcohol: Synthesis, Characterization, Crystal Structure, and Thermal Studies of an Amido Alcohol, a New Oximino Alcohol Ligand, and its Metal Complexes

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In this study, a novel reaction was observed between isonitrosoacetophenone and 1-phenylethanol amine. Acetophenone was used as a starting material to synthesize isonitrosoacetophenone by reaction of acetophenone with *n*-butyl nitrite in the presence of sodium ethoxide and to synthesize 1-phenylethanol amine by reduction of isonitrosoacetophenone with $LiAlH_4$ in diethyl ether. When the isonitrosoacetophenone reacted with 1-phenylethanol amine, (3*E*)-3-aza-5-(hydroxyimino)-1,4-diphenylpent-3-en-1-ol monohydrate, a new oximino alcohol ligand and amido alcohol were obtained as associated product interestingly. Four complexes were prepared by treatment of oximino alcohol with metal salts such as Cu^{II}, Ni^{II}, Zn^{II}, and Co^{II}. Amido alcohol was characterized by single-crystal x-ray diffraction, and all complexes were characterized by using spectroscopic techniques and thermogravimetric analysis (TGA).

Keywords amido alcohol, oximino alcohol, reduction

INTRODUCTION

Oximes are becoming increasingly important as analytical, biochemical, and antimicrobial reagents. In addition, they have received much attention due to their use as liquid crystals and dyes. The oximes of various types, such as imine-oxime, oximino alcohol, α-dioximes, α-keto oximes, amino oximes, etc., generally form colored soluble or very slightly soluble chelates with some transition metal salts, which can be used for different analitical purposes.[1–3] In recent years, dioximes, imine-oxime ligands, and complexes have been extensively studied since these structural units are thought to be involved in a variety of biochemical and industrial processes.[4,5]

The Cu^{II} and Ni^{II} complexes have been extensively studied in recent years.[6,7] During the last decade great attention was given to the area of multinuclear complexes with extended bridges,[8] mainly because of the need to gain insight into the electron transfer pathways in biological systems.[9] The homomultinuclear copper complexes of macro cyclic or macro acyclic ligands have been reported to undergo redox reactions similar to the active site in several metalloproteins, and they were also proved to be efficient catalysts under mild conditions.[10] In order to elucidate the factors that determine the function and activation of metalloproteins, several works have focused on the understanding of the correlation between the active site of metalloproteins with their metallocenters.[11]

Various methods of amide synthesis were developed. For instance, amide is commonly formed as a product after the reaction of a carboxylic acid with an amine. Cyclic amide is synthesized in the Beckmann rearrangement from oximes and amides. It is also formed by ketones and hydrazoic acid in the Schmidt reaction.[12] In this work, the synthesis of an oximino alcohol ligand (**3**) was performed by the reaction of isonitrosoacetophenone (**1**) with 1-phenylethanol amine (**2**), and its Cu^{II}, Ni^{II}, Zn^{II}, and Co^{II} complexes are explained in detail through this paper. Amido alcohol (**4**) was obtained as an unexpected product during the formation of oximino alcohol by a novel method. The synthesized oximino and amido alcohol were characterized by ^{1}H-nuclear magnetic resonance (NMR), ^{13}C-NMR, mass spectra, infrared spectra, and ultraviolet–visible (UV-VIS) spectroscopy. Amido alcohol structure was determined by single-crystal x-ray diffraction. Elemental analysis, UV-VIS spectroscopy, atomic absorption spectroscopy, mass spectra, infrared (IR) spectra, thermogravimetric analysis (TGA), and magnetic susceptibility were also used for the characterization of the complexes.

Received 13 October 2010; accepted 21 February 2011.

This work was supported by Uludag University, Scientific Research Projects Unit grant number 2009/21. The authors are grateful for this support.

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EXPERIMENTAL

Materials and General Methods

All solvents, acetophenone, and metal salts $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, and $Zn(CH_3COO)_2$ were reagent grade and used without further purification. Isonitrosoacetophenone and 1-phenylethanolamine were synthesized according to procedures described in literature.[13,14] IR spectra (4000–400 cm^{-1}) were recorded on a Thermo Nicolet 6700 FT-IR spectrometer using the KBr pellet technique. ^1H- and ^{13}C-NMR spectra of the 1-phenylethanolamine, amido alcohol, ligand, and its Zn^{II} complex in DMSO-d_6 were recorded on a Varian Mercury Plus 400-MHz NMR spectrometer at room temperature using tetramethylsilane (TMS) as internal standard. The thermogravimetric/differential thermal analysis (TG–DTA) measurements were obtained using a SII Exstar TG/DTA 6200 thermal analyzer in dry air atmosphere within the temperature range of 25–1000°C. The heating rate was 10°C min^{-1} and sample weights ranged from 5 to 10 mg. Electronic spectra were obtained on a Ati-Unicam UV2 UV-VIS spectrophotometer at room temperature. Mass spectrum, metal contents in complexes, and elemental analyses were investigated at the Laboratories of Scientific and Technological Research Council of Turkey (TUBITAK). The metal contents of the complexes were determined with atomic absorption spectroscopy. Magnetic properties were determined by a Sherwood Scientific MK1 model Gouy magnetic susceptibility balance. Molar conductivities of 10^{-3} M solutions of the complexes in methanol were measured on the WTW model inoLab 730 conductivity meter. Melting points were measured on a Büchi Melting Point B-540 digital melting point apparatus without being corrected.

Synthesis of Isonitrosoacetophenone (1) and 1-Phenylethanol Amine (2)

Isonitrosoacetophenone was synthesized by reaction of acetophenone with *n*-butyl nitrite in presence of sodium ethoxide,[13] and 1-phenylethanol amine was obtained by reduction of isonitrosoacetophenone with $LiAlH_4$ in diethyl ether.[14]

Synthesis of (3*E*)-3-Aza-5-(hydroxyimino)-1,4-diphenylpent-3-en-1-ol Monohydrate, Oximino Alcohol (3), and Amido Alcohol (4)

A solution of 1-phenylethanolamine (5 mmol, 0.685 g amine in 10 mL ethanol) was added dropwise to a solution of isonitrosoacetophenone (5 mmol, 0.745 g in 20 mL ethanol) for 20 min at room temperature. After the reaction mixture had been stirred for 5 h at the same temperature, the solution was left overnight at 0°C. The yellow crystallized product (3*E*)-3-aza-5-(hydroxyimino)-1,4-diphenylpent-3-en-1-ol monohydrate, oximino alcohol, was filtered, washed with diethyl ether, and dried in air. Filtrate was removed by evaporation. The oily product was dissolved in 1:1 ethanol:water and precipitated. The obtained crystalline material (amido alcohol) was filtered, washed with diethyl ether, and dried in air (Figure 1). Oximino alcohol was soluble in methanol, ethanol, isopropyl alcohol, and chloroform, but insoluble in hexane and diethyl ether (isolated yield: 0.672 g (50%), m.p.: 70.9°C with decomposition). Amido alcohol was soluble in methanol, ethanol, isopropyl alcohol, and chloroform, but insoluble in diethyl ether, water, and dichloromethane (isolated yield: 0.108 g (9%), m.p.: 148.3°C).

Preparation of Complexes

All of the complexes were prepared by the reaction of the oximino alcohol ligand (**4**) (2 mmol, 0.572 g) in 20 mL ethanol with the corresponding metal salts (2 mmol; 0.475 g, 0.476 g, 0.341 g, and 0.367 g, for $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, and $Zn(CH_3COO)_2$ salts, respectively) in 10 mL ethanol at room temperature over 2 h. (The pH of the reaction mixture was around 3.5–4.0 and then was adjusted to 5.5–6.0 by adding 1% NaOH solution, except for the Zn^{II} complex.) The resulting precipitate was filtered off and washed several times with ethanol and dried over calcium chloride under vacuum.

X-Ray Structure Determination

Intensity data for the title compound was collected using a STOE IPDS 2 diffractometer with graphite-monochromated (Mo-Kα radiation, $\lambda = 0.71073$ Å) at 120 K. The structure was solved with SHELXS-97[15] and refined using SHELXL-97.[16] All the nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included using a riding model in idealized positions. The details of data collection, refinement and crystallographic data are summarized in Table 1.

RESULTS AND DISCUSSION

Synthesis

Isonitrosoacetophenone (**1**) and 1-phenyl ethanolamine (**2**) were obtained as mentioned in the literature.[13,14] Oximino alcohol ligand (**3**) was synthesized by reaction of isonitrosoacetophenone with 1-phenylethanol amine as mentioned in moderate yield (50%). After separating the oximino alcohol ligand from the reaction mixture, the filtrate was evaporated and then the oily product was recrystallized, so the unexpected product, amido alcohol (**4**), was obtained at very low yield (9%). Stable solid metal complexes were synthesized by interaction of metal salts with the oximino alcohol ligand in ethanol (yields between 72 and 86%).

Crystal Structure Description

Analytical data (C, H, and N contents) are consistent with the proposed empirical formulas, also confirmed by single crystal x-ray diffraction analysis for amido alcohol. The molecular structure of amido alcohol with the atom labeling is shown in Figure 2, and selected bond lengths and angles together with hydrogen bonding geometry are listed in Tables 2 and 3. The C(7)-O(1) distance of 1.250 Å is consistent with a carbonyl C=O bonding. This value is higher than expected due to the strong

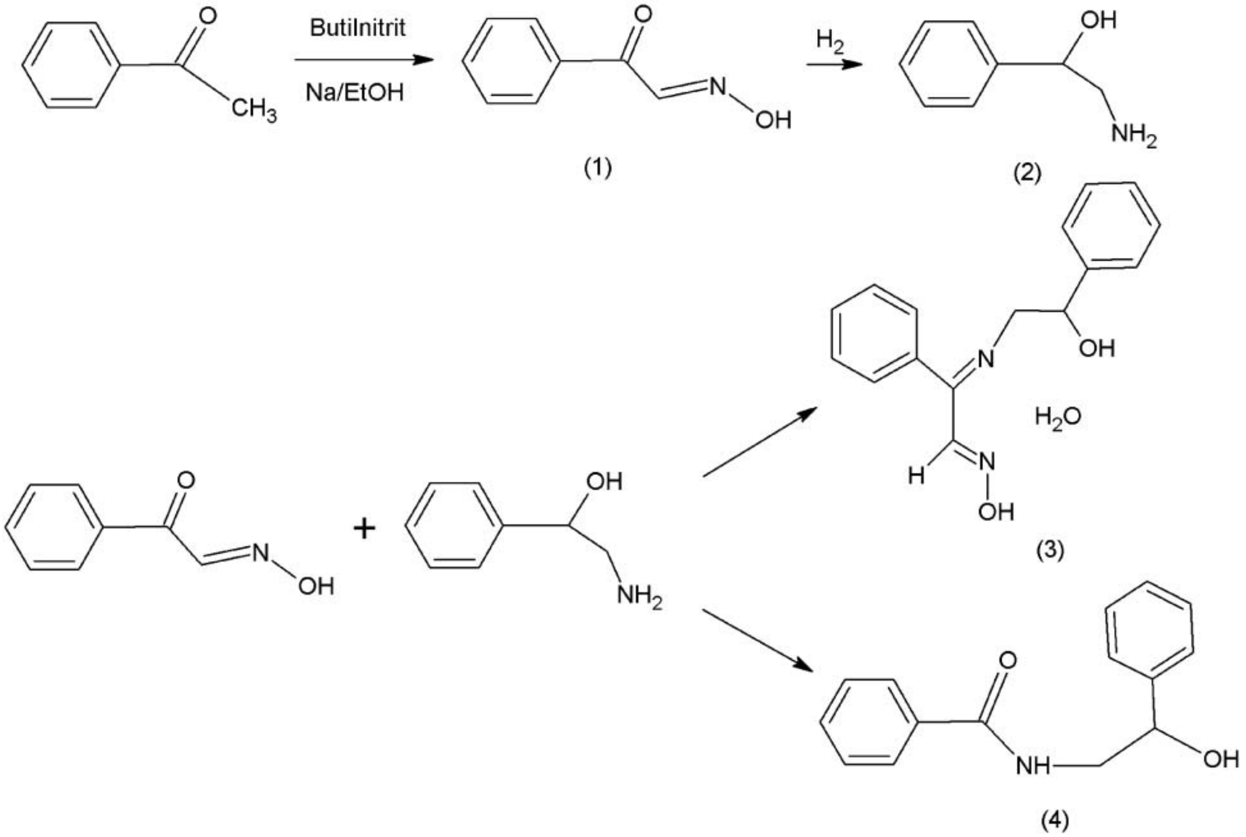


FIG. 1. The illustration of the synthesis of the oximino alcohol ligand and amido alcohol.

intermolecular hydrogen bond. The molecular structure of amido alcohol has two intermolecular hydrogen bondings: One intermolecular hydrogen bond, the length of which is 2.14 Å, is between the oxygen atom O(1) of carbonyl group and hydrogen atom of an amide group belonging to neighbor molecule N(1)-H. Another intermolecular hydrogen bond, the length of which is 1.95 Å, also exists between carbonyl oxygen O(1) and the alcohol hydrogen of the other neighboring molecule O(2)–H.

Infrared Spectra

In general, the complexes exhibit very comparable IR behavior with similar structure.[17-19] Relevant bands are given later, in Table 5. In the IR spectrum of oximino alcohol ligand (**3**), the O-H, $C{=}N_{imine}$, $C{=}N_{oxime}$, and N-O stretching vibrations are observed at 3198, 1633, 1597, and 1016 cm^{-1}, respectively. The band at 1112 cm^{-1} corresponds to the alcoholic C–O stretching vibration of the synthesized ligand. Additionally, the peak, centered at around 2612 cm^{-1} and very broad, indicates an

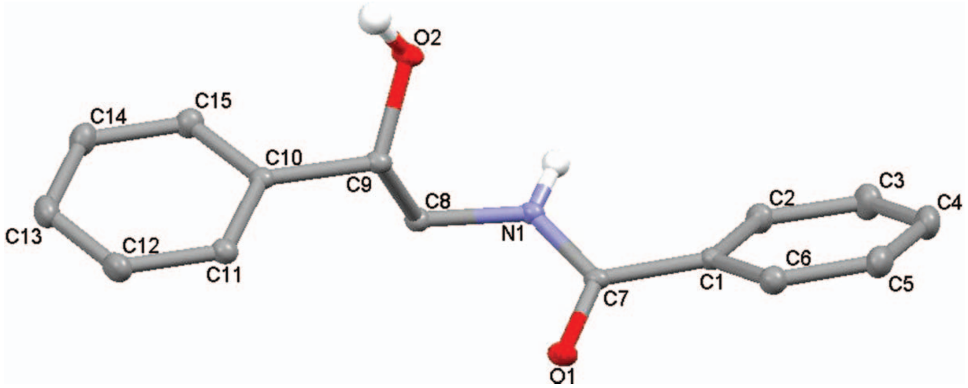


FIG. 2. The crystal structure of amido alcohol (color figure available online).

TABLE 1
Crystallographic data for amido alcohol

Empirical formula	$C_{15}H_{15}NO_2$
M_r	241.28
T (K)	293 (2)
Diffractometer	Stoe IPDS-II
Radiation, λ (Å)	Mo Kα / 0.71073 Å
Crystal system	Ortorombic
V (Å^3)	2631.58(19)
Z	8
Unit cell dimensions	
a (Å)	9.1557(3)
b (Å)	29.1108(11)
c (Å)	9.8735(5)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
D_c (mg m^{-3})	1.218
θ range (°)	1.40–25.69
Index range (h, k, l)	–11/11, –35/35, –11/11
Reflections collected ($I > 2\alpha$)	2489
Independent reflections (Rint)	1535
R	0.1233
wR	0.1157
Goodness of fit on F^2	1.143

intra- or intermolecular hydrogen bond in the ligand. The $C{=}N_{imine}$, $C{=}N_{oxime}$, and N-O stretching vibrations in the complexes are observed at 1617–1626, 1594–1597, and 1020–1064 cm^{-1}, respectively. The υ(C=N) bands shift to a lower region when the spectra of the complexes are compared with that of the oximino alcohol ligand. These results indicate that the imine and oxime nitrogen coordinate to the metal ion.[17,18] Besides, the C-O stretching vibrations in the Cu^{II}, Ni^{II}, and Co^{II} complexes are observed at 1135–1144 cm^{-1}. The bands shift to higher wavenumber by 23–29 cm^{-1} due to O–metal coordination, and this result indicates that the alcohol loses its proton.[19] In the Zn^{II} complex, there exists a C-O stretching band at 1118 cm^{-1}. This result indicates that the alcohol doesn't lose its proton. This situation is also supported by ^{1}H-NMR. The N-O band of the Zn^{II} complex is observed at the same wavenumber as the ligand's band, so it can be considered that the oxime group of ligand may lose its proton and may bond from the oxygen atom to the metal ion in the Zn^{II} complex. The carbonyl peak around 1651 cm^{-1} indicates that acetate anion was successfully incorporated into the complex. The presence of a broad absorption band centered at 3453–3500 cm^{-1} in the IR spectra of the oximino alcohol ligand and Ni^{II}, Co^{II}, and Cu^{II} complexes (**5–7**) is evidence of the presence of water molecules. The O-H characteristic peak belonging to Ni^{II}, Co^{II}, and Cu^{II} complexes was overlapped by water molecules, so O-H peaks belonging to the oxime couldn't be seen. This interpretation is also supported by IR, NMR, elemental analyses, and thermogravimetric analysis (Tables 4–6).

TABLE 2
Selected bond lengths and angles for amido alcohol

Bond lengths (Å)		Bond angles (°)	
C1−C2	1.380(4)	C1-C2-C3	120.1(4)
C2−C3	1.387(5)	C2-C1-C7	123.3(3)
C3−C4	1.374(6)	C3-C4-C5	119.8(4)
C1−C7	1.482(4)	C6-C1-C7	118.1(3)
C7−O1	1.250(3)	O1-C7-C1	120.4(2)
C7−N1	1.329(3)	O1-C7-N1	121.5(3)
C8−N1	1.457(4)	C7-N1-C8	122.6(2)
C8−C9	1.521(4)	N1-C8-C9	111.7(2)
C9−O2H	1.423(3)	O2-C9-C8	105.9(2)
C9−C10	1.507(4)	C9-O2-H15	108.0(2)
C10−C15	1.380(4)	C7-N1-H4	119.0(2)
C14−C15	1.373(5)	N1-C8-H3	109.1(15)
C13−C14	1.378(5)	C11-C10-C15	116.0(2)

TABLE 3
Hydrogen bonding geometry for amido alcohol

D−H···A	D−H (Å)	H···A (Å)	D····A (Å)	(D−H···A) (°)
N1-H4···O1^{i}	0.81(3)	2.14(3)	2.902(3)	158(3)
O2-H15···O1^{ii}	0.84(3)	1.95(4)	2.785(3)	169(3)

Symmetry codes: (i) x – 1/2, y, –z + 3/2; (ii) x – 1/2, –y + 1/2, –z + 1.

In the IR spectrum of amido alcohol (**4**), the C=O, N–H, and O–H stretching vibrations are observed at 1612, 3308, and 3405 cm^{-1}, respectively.

NMR Spectra

The ^{1}H- and ^{13}C-NMR spectra of the compounds (**1**), (**2**), (**3**), (**4**), and (**8**) are recorded using DMSO-d_6 as the solvent (Table 6). The ^{1}H- and ^{13}C-NMR spectral studies give important clues concerning the structures. ^{1}H-NMR spectrum of the isonitrosoacetophenone (**1**) clearly demonstrates the presence of a C=N–OH environment at 11.73 ppm, but this proton cannot be observed in (**3**) and (**8**).[20] At the same time, the alcoholic OH proton of the ligand doesn't appear, so we think that O-H peaks are shielded by the H_2O peak. The azomethine (CH=N) protons for the compounds (**1**), (**3**), and (**8**) appear at 8.01, 8.00, and 8.03 ppm, respectively. When the values of the chemical shifts for the compounds (**1**), (**3**), and (**8**) are compared, it can be seen that there is not any great difference among them. The appearance of a signal at 5.51 and 8.11 ppm may be assigned to the existence of –OH group of (**4**) and (**8**), respectively. The result for the Zn^{II} complex (**8**) shows that the alcohol group of the oximino alcohol ligand doesn't lose its proton and bonds

TABLE 4
Some analytical data and physical properties of the ligand, amido alcohol, and complexes

Compound	Color	Λ_M (Ω^{-1} cm^2 mol^{-1})	m.p. (°C)	Yield (%)	Formula weights (g mol^{-1})	Elemental analyses (%) found (calculated)			
						C	H	N	M
$H_2L.H_2O$ (**3**)	Yellow	6.3	70.9^d	50	286.3	66.42 (67.08)	6.02 (6.29)	9.41 (9.79)	—
Amido alcohol (**4**)	White	—	148.3	9	241.3	69.67 (69.70)	5.87 (5.80)	5.73 (5.80)	—
$NiHLCl\cdot H_2O$ (**5**)	Green	3.7	245.0^d	82	379.5	50.72 (50.51)	4.29 (4.47)	7.58 (7.40)	15.25 (15.55)
$CoHLCl\cdot H_2O$ (**6**)	Brown	5.3	185.6^d	76	379.7	50.76 (50.51)	4.19 (4.47)	7.51 (7.40)	14.15 (15.55)
$Cu_2(HL)_2Cl_2\cdot H_2O$ (**7**)	Green	19.1	117.4^d	86	750.6	51.68 (51.23)	4.22 (4.27)	7.24 (7.47)	16.17 (16.93)
$ZnHLCH_3COO$ (**8**)	Yellow	5.1	129.1^d	72	391.7	55.17 (55.21)	4.64 (4.60)	7.60 (7.21)	16.47 (16.62)

[d] Decomposition point.

TABLE 5
Characteristic IR bands (cm^{-1}) of the ligand, amido alcohol, and complexes

Compound	$\nu(NH_2)$	$\nu(OH)$	$\nu(OH_2)$	$\nu(CH)_{arom}$	$\nu(CH)_{aliph}$	$\nu(C{=}O)$	$\nu(C{=}N)$	$\nu(C–O)$	$\nu(NO)$
Isonitrosoacetophenone (**1**)	—	3272br	—	3011m	2894m	1678s	1599s	—	985s
1-Phenyl ethanolamine (**2**)	3387s, 3358m	2700br	—	3028w	2918w	—	—	1065s	—
$H_2L\cdot H_2O$ (**3**)	—	3198s, 2612br	3500br	3058w	2920w	—	1633s 1597s	1112s	1016s
Amido alcohol (**4**)	ν (NH) 3308s	3405s	—	3055w	2935w	1612s	—	1073s	—
$NiHLCl\cdot H_2O$ (**5**)	—	—	3405br	3052w	2917w	—	1618s 1596m	1135s	1041m
$CoHLCl\cdot H_2O$ (**6**)	—	—	3453br	3053w	2924w	—	1625m 1596m	1145s	1064m
$Cu_2(HL)_2Cl_2\cdot H_2O$ (**7**)	—	—	3430br	3059m	2933 w	—	1626s1597s	1138s	1036w
$ZnHLCH_3COO$ (**8**)	—	3403br	—	3060w	2925w	1651m	1617m 1594s	1118s	1020m

s: Strong, m: medium, w: weak; br: broad.

TABLE 6
^{1}H- and ^{13}C-NMR spectral data (ppm) of the ligand, amido alcohol, and Zn^{II} complex

Compounds	^{1}H-NMR spectra						
	O–H	C–H$_{alde}$	C–H$_{arom}$	C–$\underline{H}$	C$\underline{H}_2$	N–H	C–$\underline{H}_3$
Isonitrosoacetophenone (**1**)	11.73 (s, 1H)	8.01 (s, 1H)	7.51–7.95 (m, 5H)				
1-Phenyl ethanolamine (**2**)	2.22 (s, 1H)	—	7.25–7.37 (m, 5H)	4.65 (m, 1H)	2.95 (m, 2H)	2.22 (s, 2H)	—
$H_2L.H_2O$ (**3**)	Not observed	8.00 (s, 1H)	7.19–7.96 (m, 10H)	4.43 (m, 1H)	2.62 (m, 2H)	—	—
Amido alcohol (**4**)	5.51 (d, 1H)	—	7.20–7.82 (m, 10H)	4.76 (m, 1H)	3.36 (m, 2H)	8.49 (t, 1H)	—
$ZnHLCH_3COO$ (**8**)	8.11 (s, 1H)	8.03 (s, 1H)	7.23–7.96 (m, 10H)	4.41 (m, 1H)	2.53 (d, 3H)	—	1.90(s,3H)
	^{13}C-NMR spectra						
	C=O	R$\underline{C}$ = NR^1	H-$\underline{C}$ = NOH	Ph($\underline{C}$–H)	$\underline{C}$–H	$\underline{C}$H$_2$	$\underline{C}$-H$_3$
Isonitrosoacetophenone (**1**)	168.7	—	148.2	128.0–134.1	—	—	—
1-Phenyl ethanolamine (**2**)	—	—	—	125.9–142.5	74.3	49.2	—
$H_2L.H_2O$ (**3**)	—	189.4	148.1	126.3–144.7	74.7	50.5	—
Amido alcohol (**4**)	166.8	—	—	126.4–144.2	71.6	48.1	—
$ZnHLCH_3COO$ (**8**)	177.7	190.7	147.8	126.0–144.2	75.6	48.1	22.3

TABLE 7

Mass spectra data, UV-VIS spectra data, and magnetic moment measurements of the ligand, amido alcohol, and complexes

Compound	MS (ESI), *m/z*	λ_{max}, nm	μ_{eff} (B.M.)
$H_2L\cdot H_2O$ (**3**)	269.1(100), 185.1(60), 172.0(10), 120.1(20)	208, 256, 268, 341	—
Amido alcohol (**4**)	241.8(40), 223.7(100), 104.8(10)	—	—
$NiHLCl\cdot H_2O$ (**5**)	381.0(5), 379.1(20), 321.0(10), 282.1(20), 223.9(100), 162.8(25)	208, 256, 275, 352, 399, 630	2.99
$CoHLCl\cdot H_2O$ (**6**)	379.9(10), 321(60), 256.0(100), 142.8(40), 108.8(25)	207, 256, 280, 354, 409	4.04
$Cu_2(HL)_2Cl_2\cdot H_2O$ (**7**)	753.8(10), 749.0(45), 521.8(15), 427.4(25), 282.1(100), 126.8(20)	210, 256, 270, 350, 428, 714	1.19
$ZnHLCH_3COO$ (**8**)	392.0(5), 391.2(15), 324.9(15), 268.9(100), 223.9(20), 149.8(50), 119.9(45)	205, 256, 272, 310, 397	Dia

from the oxygen atom to the metal ion. At the same time, the CH_3 protons at 1.90 ppm demonstrate that acetate anion participates in the Zn^{II} complex. Aromatic C–H protons are observed at 7.20–7.96 ppm in all of the structures. The N-H proton appears at 8.49 ppm in compound (**4**). In the ^{13}C-NMR spectrum of (**4**), carbonyl carbon is observed 166.8 ppm and the signals of the $C_{aromatic}$ carbon are observed at 126.4–144.2 ppm.[21] In the ^{13}C-NMR spectrum of compound (**3**), the signals of the carbon atoms of azomethine groups appear at 189.4 and 148.1 ppm. The signals of the $C_{aromatic}$ carbon are observed at 126.5–144.7 ppm. The peaks of $\underline{C}$-H and $\underline{C}$-H_2 appear at 74.7 and 50.5 ppm, respectively.[22] In compound (**8**), the signal of the carbon atom of imine group appears at 190.7 ppm. This shows that the ligand bonds from the imine nitrogen atom to the metal ion in the Zn^{II} complex. Carbonyl carbon and $\underline{C}H_3$ carbon are also seen at 177.7 and 22.3 ppm. It is concluded that acetate anion participates in the Zn^{II} complex. The ^{1}H- and ^{13}C-NMR spectral data support the proposed structures and indicate the formation of the amido alcohol, oximino alcohol ligand, and its Zn^{II} complex.

Mass Spectra

The mass spectra (electrospray ionization, ESI) of oximino alcohol ligand and amido alcohol exhibit a molecular ion at *m/z* 269.1 (268.3) $[M\text{-}H_2O]^+$, which indicates the formation of the ligand, and a molecular ion at *m/z* 241.8 (241.3) $[M]^+$, which indicates the formation of the amido alcohol. The molecular ion peaks appear at (*m/z*, ESI) 379.1(378.0) $[M]^+$, 379.9(379.0) $[M]^+$, 749.0(748.0) $[M]^+$, and 391.2(390.0) $[M]^+$ for the Ni^{II}, Co^{II}, Cu^{II}, and Zn^{II} complexes, respectively (Table 7).[6] There are two or more isotopes for Ni, Cu, Zn, and chlorine, so mass spectra of these complexes have been observed with isotopic effects. For instance, there are tree isotopes of copper and two isotopes of chlorine, with ^{63}Cu (69%) and ^{35}Cl (76%) being the most abundant isotopes, so two peaks 749.0 (45) and 753.8(15) are observed in the Cu^{II} complex.

Electronic Spectra

The electronic spectra of the ligand and complexes are recorded in chloroform at room temperature (Table 7). Electronic spectral data show π–π^* transitions relating to the benzene ring at 205–256 nm, imine π–π^* transition at 268–280 nm, and imine n–π^* transition at 310–354 nm. In the complexes, imine π–π^* and n–π^* transitions shift to longer wavelengths after complexation, so this confirms the imine nitrogen is coordinated to the metal atom.[23] Ni^{II} and Cu^{II} complexes reveal a less intense shoulder at 630 nm ($\varepsilon = 130$ L mol^{-1} cm^{-1}) and 714 nm ($\varepsilon = 470$ L mol^{-1} cm^{-1}), assigned to d–d transitions of the metal ions, respectively. The weak d–d transition couldn't be observed in the Co^{II} complex. Because the d–d transition may shift the UV region, this band may remain below the charge transfer transition. Five coordinated Cu^{II} complexes showing absorption in the 588–769 nm region approximate a square pyramidal geometry, while complexes with a trigonal bipyramidal geometry show absorption bands in the 685–952 nm region, with highest absorption intensities in the range 666–877 nm.[24,25]

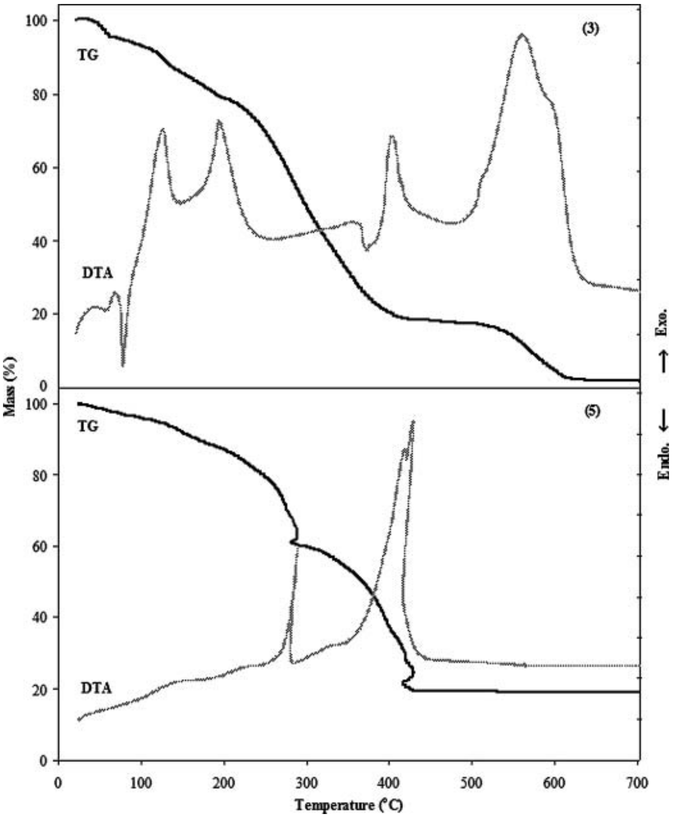
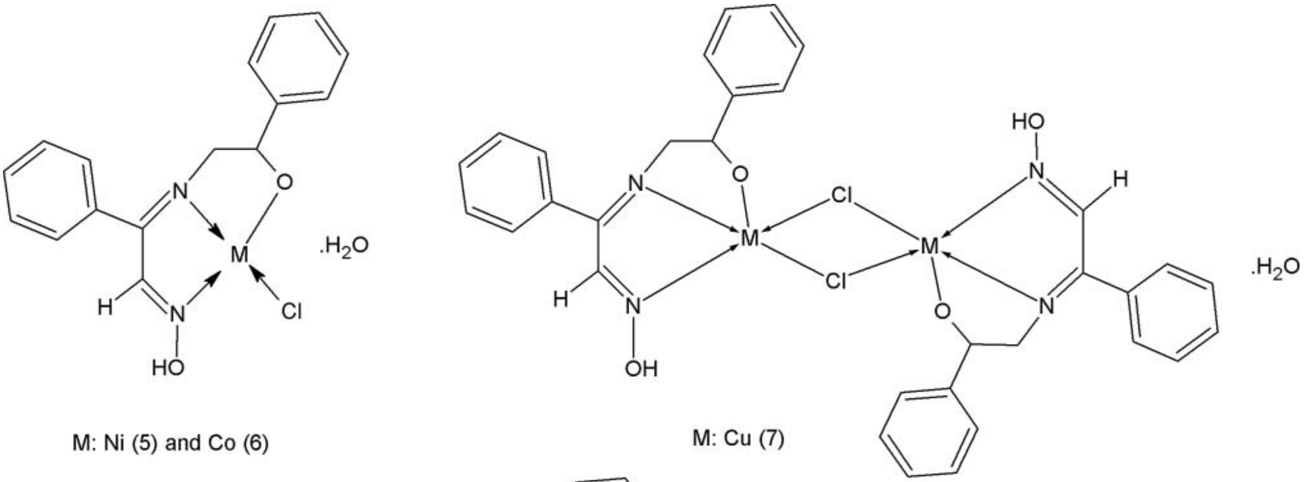


FIG. 3. DTA and TG curves of oximino alcohol (**3**) and its Ni^{II} complex (**5**)

TABLE 8
Thermal decomposition of the ligand and complexes

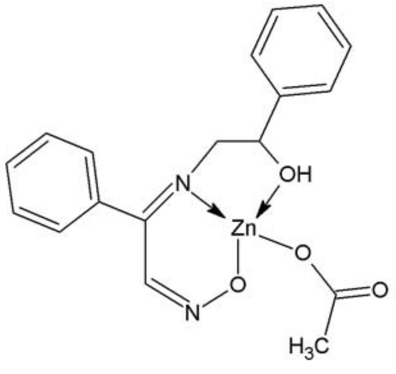
Compound	Step	Temperature range (°C)	DTA$_{max.}$ (°C)	Mass loss (%) found (calculated)	Residue (%) found (calculated)	Leaving group	Decomposition product
$H_2L \cdot H_2O$ (**3**)	1	28–76	56(+)	6.10 (6.25)	93.90 (93.71)	H_2O	H_2L
	2	77–192	126(–), 190(–)	15.32			(L:$C_{16}H_{16}N_2O_2$)
	3	193–422	340(–), 402(–)	50.56			
	4	423–647	559(–), 593(–)	26.12	1.90 (0)	H_2L	—
$NiHLCl \cdot H_2O$ (**5**)	1	32–101	83(+)	4.12 (4.74)	95.88 (95.26)	H_2O	NiHLCl
	2	102–288	233(–), 274(–)	35.28			
	3	289–461	395(–), 401(–)	41.04	19.56 (19.76)	HLCl	NiO
$CoHLCl \cdot H_2O$ (**6**)	1	46–124	92(+)	4.25 (4.74)	95.75 (95.26)	H_2O	CoHLCl
	2	125–208	186(–)	35.71			
	3	209–518	362(–), 375(–)	40.02	20.02 (19.76)	HLCl	CoO
$Cu_2(HL)_2Cl_2 \cdot H_2O$ (**7**)	1	51–95	78(+)	2.13 (2.40)	97.87 (97.60)	H_2O	$Cu_2(HL)_2Cl_2$
	2	96–202	122(–)	24.81			
	3	203–392	267(–), 300(–)	24.57			
	4	393–594	486(–)	28.70	20.28 (21.20)	2 HLCl	CuO
$ZnHLCH_3COO$ (**8**)	1	49–218	140(–)	17.17 (15.08)	82.83 (84.92)	CH_3COO	ZnHL
	2	219–442	415(–)	38.59			
	3	443–530	483(–)	25.08	19.16 (20.72)	HL	ZnO

(+) : endothermic, (–): exothermic.



M: Ni (5) and Co (6)

M: Cu (7)



(8)

FIG. 4. The schematic illustration of related metal complexes.

The electronic spectrum of the Cu^{II} complex has agreed with a square pyramidal structure, which is confirmed by structural studies.[26] Additionally, d–d transition of the metal ion is probably due to the $^3A_2 \rightarrow {}^3T_2$ (F) transition of tetrahedral geometry for Ni^{II} complex.[27] The spectra of all the complexes show an intense band at $\sim$397–428 nm ($\varepsilon = 1.08$–1.96×10^4 L mol^{-1} cm^{-1}), which can be assigned to charge transfer (CT) transition of tetrahedral geometry.[28]

Magnetic Susceptibility and Molar Conductance Studies

The magnetic moments of the complexes are investigated at room temperature (Table 7). Magnetic susceptibilities of Ni^{II}, Co^{II}, and Cu^{II} complexes are measured as 2.99, 4.04, and 1.19 B.M., respectively. As expected, the Zn^{II} complex doesn't show any magnetism. It is obvious that the Cu^{II} complex possess antiferromagnetic properties at room temperature, shown by strong intramolecular antiferromagnetic spin exchange interaction as reported previously for di- and trinuclear Cu^{II} complexes with oximate bridged ligands.[29,30] The measurements of the magnetic susceptibility of the complexes having d^8 and d^7 configurations show that the complexes may have tetrahedral or tetragonal structures for Ni^{II} and Co^{II} complexes, and these results are well adjusted with the previous studies.[28,31]

The molar conductance values of the synthesized oximino alcohol ligand and its Cu^{II}, Ni^{II}, Zn^{II}, and Co^{II} complexes are in a range from 3.7 to 19.1 Ω^{-1} cm^2 mol^{-1} in methanol solutions, indicating the nonelectrolyte nature of these compounds.[32] These values provide some indication to support our proposed structural conformation for complexes.

Thermogravimetric Analysis

Thermal decompositions of metal complexes of oximino alcohol ligand are examined by thermogravimetric (TG) analyses in the temperature range of 25–1000°C. The TG and differential thermal analysis (DTA) curves of oximino alcohol (**3**) and its Ni^{II} complex are illustrated in Figure 3, and the thermoanalytical results obtained from TG and DTA curves for all these compounds are given in Table 8. The decomposition temperature and the weight losses of the complexes are calculated from TGA data. Ligand and all the complexes lose adsorbed water between 28 and 124°C,[33] and then the decomposition is complete at 647°C for all the compounds. The data obtained from the thermogravimetric analyses indicate that the decomposition of the ligand and complexes proceeds in three or four steps. All complexes undergo complete decomposition to the corresponding metal oxides, CoO, NiO, CuO, and ZnO.[34]

Metal complexes have not been isolated as a crystalline product for x-ray diffraction studies. Therefore, the structural studies of the ligand and their complexes were done by spectroscopic methods.

CONCLUSIONS

A new oximino alcohol ligand was prepared via condensation reaction between α-carbonyl oxime and 1-phenylethanol amine. We reported the oximino alcohol's complexes with the appropriate transition metal ions such as Cu^{II}, Ni^{II}, Zn^{II}, and Co^{II}. Spectroscopic measurements and magnetic moment studies showed that Ni^{II}, Co^{II}, and Zn^{II} complexes have high-spin distorted tetrahedral configuration, Cu^{II} complexes have square pyramidal configuration, and the Cu^{II} complexes possess antiferromagnetic properties by strong intramolecular antiferromagnetic spin exchange interaction, so we suggested a dinuclear structure for the Cu^{II} complex. These complexes may serve as models of relevance to bioinorganic chemistry such as metalloenzymes. The infrared, UV-VIS, elemental analyses, and magnetic moment studies suggest that the azomethine nitrogen, oxime nitrogen, and deprotonated alcoholic oxygen atom of the oximino alcohol ligand are coordinated and covalently bonded to metal atoms in the Ni^{II}, Co^{II}, and Cu^{II} complexes and the azomethine nitrogen, deprotonated oxime oxygen, and alcoholic oxygen atom of the oximino alcohol ligand are coordinated and covalently bonded to metal atoms in the Zn^{II} complex (Figure 4). Thus, the oximino alcohol ligand behaves as tridentate.

It was observed that amido alcohol was obtained as associated product during the reaction. This structure was characterized with spectroscopic and single-crystal x-ray diffraction methods. In conclusion, we determined that the reaction between isonitrosoacetophenone and 1-phenyl ethanolamine was very novel.

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