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The Synthesis and Characterization of 1,2-Dihydroxyimino-3,6-di-aza-8,9-O-iso-butylidene Nonane and Its Complexes with Ni(II), Cu(II), Zn(II) and Cd(II)

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1,2-Dihydroxyimino-3,6-di-aza-8,9-O-iso-butylidene nonane (H_2L) was synthesized starting from 1,2-O-iso-butylidene-4-aza-6-amino hexane (RNH_2) and antichloroglyoxime. Ni(II) and Cu(II) complexes of H_2L have a metal:ligand ratio of 1:2 and the ligand coordinates through two N atoms, as do most of the vic-dioximes. However, Zn(II) and Cd(II) complexes of H_2L have a metal:ligand ratio of 1:1 and one chloride ion and one water molecule are also coordinated to the metal ion. Structures of the ligand and its transition-metal complexes are proposed, according to elemental analyses, IR, ^{13}C and ^1H NMR spectra, magnetic susceptibility measurements and thermogravimetric analyses (TGA).

Key words: vic-dioxime, Ni(II), Cu(II), Zn(II), Cd(II) complexes

The coordination chemistry of vic-dioxime is an intensive area of study and numerous transition-metal complexes of this group of ligands have been investigated [1,2]. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure, which is stabilized by hydrogen bonding [3]. The complexes prepared by vic-dioximes have been extensively used for various purposes, owing to the high stability of these compounds, including model compounds for vitamin B_{12} or analytical reagents [4,5]. Vic-dioximes, containing mildly acidic hydroxy groups and slightly basic nitrogen atoms, are amphoteric and their transition metal complexes have been widely investigated as analytical reagents [4]. The geometrical isomers of vic-dioximes and their derivatives, depending on the position of the -OH groups in the molecule, are syn-, anti- and amphi-structures, usually, the stability order of these is anti> amphi> syn configuration [6,7], but there are some exceptions [8,9]. The anti- and amphi-forms of these isomers give two different coloured complexes with the same metal, but the syn-form does not form complexes [8].

Several mono- and disubstituted aminoglyoximes have been synthesized from anti-chloroglyoxime, anti-chlorophenylglyoxime or anti-dichloroglyoxime with corresponding amines and their transition metals complexes have been isolated [10–23]. In the present paper, we report the synthesis and characterization of a new vic-dio-

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*Address for correspondence to Mehmet KAYA: E-mail: kayam08@yahoo.com xime ligand and its complexes with Ni(II), Cu(II), Zn(II) and Cd(II) ions. As far as we know, this is the first report on this ligand.

EXPERIMENTAL

The preparation of anti-chloroglyoxime has been described previously [24]. All the reagents used were purchased from Merck or Fluka or Sigma Company and are chemically pure.

Physical measurements: Elemental analyses (C, H, N) were performed on a LECO-932 CHNSO elemental analyses apparatus. IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets and NaCl cell. ^{13}C and ^{1}H NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR and a Jeol FX 90 Q FT-NMR Spectrometers. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temprature (20°C), using $Hg[Co(SCN)_2]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [25]. The metal contents of the complexes were determined with an Anti Unicam (Model 929) atomic absorption spectrophotometer in solutions, prepared by decomposition of the compounds in conc. HCl and conc. HNO_3 (3:1) solution followed by dilution in water. TGA curves were recorded on a Shimadzu TG-50 thermobalance.

Synthesis of 1-chloro-2,3-O-iso-butylidene propane (1): 15–20 drops of borontrifluoride etherate were added dropwise to 36.15 g (500 mmole) of purified methyl ethyl ketone. Then 23.10 g (250 mmole) of epichlorohydrine was added dropwise to the mixture at 15–20°C while it was stirred. After addition of epichlorohydrine, the reaction mixture was further stirred for 3 h at 20°C. The liquid product was distilled at 60–65°C and 35 mm-Hg in vacuum. Yield: 66%; IR bands (NaCl cell, cm^{-1}): 757 ν(C–Cl), 2978–2876 $\nu(C\text{–}H)_{aliph.}$, 1089 δ(C–O–C); ^{1}H NMR (DMSO-d_6, δ ppm, 90 MHz): 1.42–1.63 (m, 2H, CH_2), 1.00–1.31 (s, 6H, CH_3), 4.00–4.41 (m, 1H, CH-O), 3.20–3.60 (m, 2H, CH_2-O), 3.60–4.08 (m, 2H, CH_2-Cl); ^{13}C NMR (DMSO-d_6, δ ppm, 90 MHz): 11.90–12.39 (C_1), 26.34 (C_2), 23.98–25.09 (C_3), 114.05 (C_4), 70.74 (C_5), 76.09 (C_6), 45.24 (C_7).

Synthesis of 1,2-O-iso-butylidene-4-aza-6-aminohexane (2): In a reaction flask, a $CaCl_2$ drying tube and a dropping funnel, 12.03 g (200 mmole) of ethylene diamine, 5.06 g (50 mmole) of triethylamine and 70 mL of absolute toluene were mixed and heated to 80°C. To this mixture, a solution of 8.41 g (50 mmole) of 1-chloro-2,3-O-iso-butylidene propane (**1**) in 35 mL toluene was added dropwise, refluxed for 30 h and cooled to room temperature. The mixture was filtered and the filtrate was evaporated to remove the excess of ethylene diamine. The compound was distilled at 95–100°C at 10 mm-Hg in vacuum. Yield: 60%; IR bands (NaCl cell, cm^{-1}): 3400 ν(–NH); ^{1}H NMR (DMSO-d_6, δ ppm, 90 MHz): 1.50–1.60 (m, 2H, CH_2), 1.00–1.20 (s, 6H, CH_3), 3.68–4.20 (m, 1H, CH-O), 3.00–3.57 (m, 2H, CH_2-O), 2.45 (m, 6H, N-CH_2-), 1.50 (s, 3H, NH deuterium exchangeable); ^{13}C NMR (DMSO-d_6, δ ppm, 90 MHz): 9.87–10.41 (C_1), 25.06 (C_2), 23.40–24.80 (C_3), 113.35 (C_4), 70.00 (C_5), 75.48 (C_6), 56.70 (C_7), 42.13 (C_8), 36.37 (C_9).

Synthesis of the ligand H_2L (3): A solution of $NaHCO_3$, 3.40 g (40 mmole), was added to a solution of 1,2-O-iso-butylidene-4-aza-6-amino hexane 5.66 g (30 mmole) in 60 mL absolute ethanol, then a solution of anti-chloroglyoxime, 3.70 g (30 mmole) in 50 mL absolute ethanol, which is synthesized by the method described previously [24], was added dropwise to the mixture at room temperature over 4 h, the mixture was stirred on a water bath at 60–70°C for 5 h. The mixture was filtered and ethanol was removed by evaporation. The oily product was dissolved in abs. chloroform and precipitated in n-hexane (1/10). Obtained product was filtered off, washed with n-hexane and water several times and dried in vacuum for 10 h. The compound found to be soluble in $CHCl_3$, DMSO, DMF and acetone and insoluble in diethyl ether and n-hexane. The yield, colour, melting point and IR bands (KBr pellet, cm^{-1}) are given in Tables 1 and 2. ^{13}C NMR (DMSO-d_6, δ ppm, 400 MHz): 8.70–8.89 (C_1), 24.80 (C_2), 23.42-23.60 (C_3), 112.00 (C_4), 68.89 (C_5), 74.42 (C_6), 48.98 (C_7), 48.14 (C_8), 39.10 (C_9), 149.13 (C_{10}), 152.39 (C_{11}).

Synthesis of the Ni(II) and Cu(II) complexes: 0.275 g (1 mmole) of the ligand was dissolved in 10 mL absolute methanol. A solution of 0.5 mmole metal salts [$NiCl_2{\cdot}6H_2O$ (0.118 g) and $CuCl_2{\cdot}2H_2O$ (0.086 g)] in 10 mL absolute methanol was added dropwise to the ligand solution with continuous stirring. The apparent pH of the solutions, 5.0–5.5, by the addition of a 1 M NaOH solution in methanol. Every mixture was stirred 2 h more at 35 °C, and the complexes thus precipitated were kept on a water bath for 35 min at 40°C, filtered and the precipitate washed with diethyl ether and water. The precipitate was dissolved in abs. methanol and precipitated in diethyl ether (1/10) and dried in vacuum at 60°C. The complexes are soluble in THF, DMF and DMSO and insoluble in diethyl ether, n-hexane and water. The yield, colour and melting point, and IR bands (KBr pellet, cm^{-1}) are given in Tables 1 and 2.

Synthesis of the Zn(II) and Cd(II) complexes: 0.276 g (1 mmole) of the ligand was dissolved in 10 mL absolute methanol. A solution of 1 mmole metal salts [$ZnCl_2$ (0.137 g) and $CdCl_2 \cdot H_2O$ (0.202 g)] in 10 mL absolute methanol was added dropwise to the ligand solution with continuous stirring. The apparent pH of the solutions, 5.0–5.5, by the addition of a 1 M NaOH solution in methanol. The mixture was further stirred on a water bath at 50°C for 2 h in order to complete precipitation. The precipitate was filtered, washed with diethyl ether. The precipitate was dissolved in abs. methanol and precipitated in diethyl ether (1/10) and dried in vacuum at 60°C. The complexes are soluble in DMF, DMSO, acetonitrile, and acetone and insoluble in diethyl ether, n-hexane and water. The yield, colour and melting point, and IR bands (KBr pellet, cm^{-1}) are given in Tables 1 and 2.

RESULTS AND DISCUSSION

1,2-Dihydroxyimino-3,6-di-aza-8,9-O-iso-butylidene nonane H_2L was prepared in a three-stage process as shown in Scheme 1. The structural characterization data of (**1**) are given in the experimental section and of (**2**) in the experimental section and Tables 1–3. The structure of H_2L was identified by using elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy techniques and thermogravimetric analyses (TGA).

In the IR spectrum of (**2**), the characteristic bands are at 3400 cm^{-1}, which are assigned to $\nu(-NH)$ and $\nu(-NH_2)$ groups, respectively and at 1089 cm^{-1}, assigned to the $\delta(C-O-C)$ group. There is no C–Cl band in the IR spectrum of (**2**). In the ^1H NMR spectra of (**2**), a peak appears at 2.45 ppm for $(N-CH_2-)$ and 1.50 ppm for (–NH and $-NH_2$) as broad peak. These peaks (–NH and $-NH_2$) disappeared upon the addition of D_2O. Observation of the $(-O-CH_2-)$ peaks at 3.00 and 3.57 ppm, as multiplets in each case, indicates that the compound undergoes *cis-trans* isomerization [15,21,26], The isomer ratios were found to be 46% *cis* and 54% *trans* from the ^1H NMR and ^{13}C NMR data.

The characterization of the ligand H_2L was carried out by elemental analyses, IR, ^1H, ^{13}C-NMR, and thermogravimetric analyses (TGA). In the IR spectrum of H_2L, characteristic peaks appear at 3380 cm^{-1} $\nu(N-H)$, 3264 cm^{-1} $\nu(O-H)$, 1630 cm^{-1} $\nu(C=N)$, 1089 cm^{-1} $\delta(C-O-C)$ and 975 cm^{-1} $\nu(N-O)$ as expected for a substituted vic-dioxime [24]. In the ^1H NMR spectrum, since the (–OH) protons of the oxime are equivalent in the (E,E) form, two peaks were observed for the protons [21,27]. In the H_2L chemical shifts of (=N–OH) protons were observed at 7.62 and 8.18 ppm as singlets. Also, chemical shifts of (N–H) protons were observed at 5.57 and 6.18 ppm. These bands are easily identified by deuterium exchange.

The C–H protons adjacent to the oxime groups were observed at about 7.80 ppm. This value is in agreement with these reported earlier [22,28]. In the ^{13}C NMR, carbon resonances of dioxime groups (C_{10} and C_{11}) were observed at 149.13 and 152.39 ppm as expected for (E,E) dioxime [17,21]. The most characteristic signal for C_4(ipso) is at 112.00 ppm.

Scheme 1

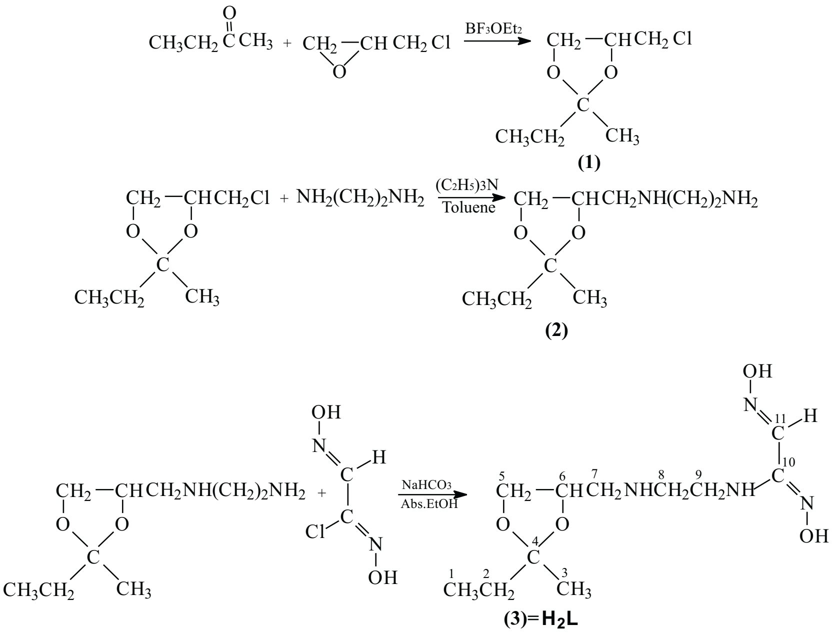

Table 1. The formulas, formula weights, colours, melting points, yields and magnetic susceptibilities of the ligand and the complexes.

Compounds	M.w g/mol	Colour	M.p °C	Yield %	μ_{eff} B.M.
R-Cl (1) **$C_7H_{13}O_2Cl$**	164.63	Colorless	–	66	–
R-NH_2 (2) **$C_9H_{20}N_2O_2$**	188.27	Colorless	–	60	–
H_2L (3) **$C_{11}H_{22}N_4O_4$**	274.37	white	99	63	–
$[(HL)_2Ni]$ **$C_{22}H_{42}N_8O_8Ni$**	605.41	tile red	201	57	dia
$[(HL)_2Cu]$ **$C_{22}H_{42}N_8O_8Cu$**	610.27	green	154	52	1.75
$[(HL)Cl(H_2O)Zn]$ **$C_{11}H_{23}N_4O_5ClZn$**	392.22	yellow	224	58	dia
$[(HL)Cl(H_2O)Cd]$ **$C_{11}H_{23}N_4O_5ClCd$**	439.24	yellow	216	59	dia

The ligand H_2L has been synthesized by the reaction of compound (**2**) and anti-chloroglyoxime. Excess sodium bicarbonate was used to neutralize the HCl liberated in the reaction. The red color for the Ni(II) complex of the H_2L indicates that the ligand is in the (E,E) form [29], the anti-form of the ligand.

Table 2. Characteristic IR bands (cm^{-1}) of the ligand and complexes as KBr pellets.

Compounds	ν(O–H)	ν(N–H)	ν(N–O)	ν(C=N)	Others
LH_2	3264	3380	975	1630	–
$[(HL)_2Ni]$	–	3358	964	1604	1739 δ(O...H–O)
$[(HL)_2Cu]$	–	3364	959	1616	1726 δ(O...H–O)
$[(HL)Cl(H_2O)Zn]$	3236	3368	983	1624	3420 (H_2O)
$[(HL)Cl(H_2O)Cd]$	3232	3372	1000	1591	3430 (H_2O)

ν(C–O–C) = 1089 cm^{-1} for all compounds.

The mononuclear complexes of H_2L with Ni(II) and Cu(II) have a metal:ligand ratio of 1:2. The infrared band observed near 1630 cm^{-1}, assigned to the ν(C=N) frequency in the free ligand, is shifted to lower frequencies (1604–1616 cm^{-1}) after complexation due to N,N-metal coordination [15,30,31]. At the same time, the band observed at 975 cm^{-1} in the free ligand, which assigned to the ν(N–O), is shifted to lower frequency after complexation (Table 2). On the other hand, a band not seen in the free ligand, which is assigned to δ(O···H–O) [31], is observed at 1739 cm^{-1} for Ni(II) and 1726 cm^{-1} for Cu(II). These absorptions indicate that the oxime group takes part in complexation. In the ^1H NMR spectrum of the Ni(II) complex, there are no OH peaks as expected for the formula in Fiqure 1, but there is a peak at 14.83 ppm for Ni(II), which is assigned to the (O···H–O) [28,31] and this result can be easily supported by deuterium exchange. The Ni(II) complex is diamagnetic, whereas the Cu(II) complex is paramagnetic and its magnetic susceptibility value is 1.75 B.M. For these complexes, additional analytical data are given in Tables 1–3**.** These results indicate a square-planar geometry for the Ni(II) and Cu(II) complexes. The suggested structure of the complexes is shown in Figure 1.

Table 3. ^1H NMR spectra of the ligand and the complexes in DMSO-d_6 in δ (ppm).

Compounds	H_2L	$[(HL)_2Ni]$	$[(HL)Cl(H_2O)Zn]$	$[(HL)Cl(H_2O)Cd]$
N–H^a	5.57–6.18 (2H)^s	5.63–6.37 (4H)^s	5.47–6.01 (2H)^s	5.45–6.00 (2H)^s
N-CH_2^{b}	2.70–3.30 (6H)^m	3.35–3.98 (12H)^m	2.84–3.40 (6H)^m	2.84–3.40 (6H)^m
–CH_2–	1.37–1.54 (2H)^m	1.30–1.50 (4H)^m	1.42–1.50 (2H)^m	1.40–1.50 (2H)^m
–CH_3–	1.16–1.24 (6H)^s	1.05–1.30 (12H)^m	1.20–1.31 (6H)^s	1.20–1.30 (6H)^s
–CH–O	4.23–4.69 (1H)^m	4.04–4.70 (2H)^m	4.00–4.72 (1H)^m	4.01–4.73 (1H)^m
–CH_2–O	3.51–4.98 (2H)^m	3.40–5.00 (4H)^m	3.62–4.99 (2H)^m	3.60–5.00 (2H)^m
N–OH^{a,b}	7.62–8.18 (2H)^s	–	8.05–9.00 (1H)^s	8.04–8.97 (1H)^s
N=C–H	7.80 (1H)^s	7.46 (2H)^s	7.96 (1H)^s	7.94 (1H)^s
(O–H...O)^a	–	14.83 (2H)^s	–	–
H_2O	–	–	3.20 (2H)^s	3.30 (2H)^s

^{s}singlet; ^{m}multiplet; ^{a}deuterium exchangeable; ^{b}broad bands.

The Zn(II) and Cd(II) complexes have a 1:1 metal:ligand ratio according to the elemental analyses and the ligand is coordinated only by the N, O atoms of the vic-dioxime [32]. Therefore, in the IR spectrum of the Zn(II) and Cd(II) complexes, the stretching band of ν(C=N) appearing at 1630 cm^{-1} in H_2L is shifted to 1624 cm^{-1} for Zn(II) and 1591 cm^{-1} for Cd(II). At the same time, the ν(N–O) band (at 975 cm^{-1} in the free ligand) was moved to higher frequency (according to H_2L) of *ca.* 15 cm^{-1} after complexation. These suggest that the ligand is coordinated to metal ions through the nitrogen and oxygen donors. A chloride ion and a water molecule are also coordinated to metal ions. A broad band at 3420–3430 cm^{-1} was observed in the spectra of the complexes, due to the coordinated a water molecule to the metal ions in the complexes. In the ^1H NMR spectrum, the Zn(II) and Cd(II) complexes show the presence of a coordinated water molecule 3.20–3.30 ppm [22] and there is no (O···H–O) peaks as expected for complexes formula in Figure 2, but there is a resonance at 8.04–9.00 ppm, which is assigned to (–OH). The suggested structure of the complexes is shown in Figure 2. The Zn(II) and Cd(II) complexes were characterized by IR, NMR, TGA and elemental analyses and leads us to consider the geometry of complexes to be tetrahedral [29].

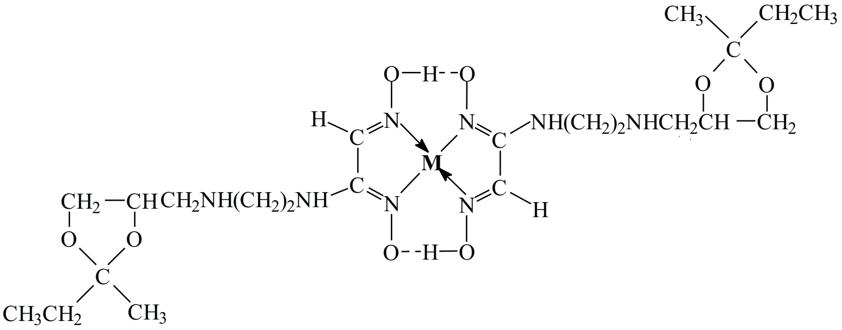

Figure 1. Suggested structure of the square-planar Ni(II) and Cu(II) complexes of the ligand.

The ^{13}C NMR spectra of the Ni(II), Zn(II) and Cd(II) complexes were similar to those of the corresponding free ligand. Upon coordination with Ni(II), Zn(II) and Cd(II) ions, the ligand resonances shifted slightly [33–35].

The thermal stabilities of the ligand and the complexes were investigated by a combination of TGA. TGA curves were obtained at a heating rate of 10°C/min in a nitrogen atmosphere over the temperature range of 25–850°C. The ligand H_2L is stable up to 117°C and its decomposition starts at 117°C and is completed at 623°C. Thermal studies show that the complexes are stable up to 190°C for $[(HL)_2Ni]$ and 146°C for $[(HL)_2Cu]$. In the TGA curve of the $[(HL)Cl(H_2O)Zn]$ complex, 4.83% weight loss was observed at 135°C. For the $[(HL)Cl(H_2O)Cd]$ complex, 4.36% weight loss was observed at 140°C. This shows that the complexes contain one mole of water for coordinated complex molecule, respectively. Elemental analysis results support the data of TGA. As can be seen in the TGA data, all the complexes and the ligand decompose in two steps at different temperature ranges. All these complexes undergo complete decomposition to the corresponding thermodynamically stable metal oxides, NiO (residue: 13.02%), CuO (residue: 12.57%), ZnO (residue: 21.3%), CdO (residue: 28.64%) [36,37].

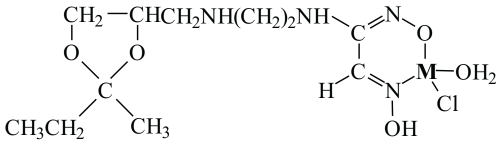

Figure 2. Suggested structure of the tetrahedral Zn(II) and Cd(II) complexes of the ligand.

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