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SYNTHESIS AND CHARACTERIZATION OF A VIC-DIOXIME DERIVATIVE AND INVESTIGATION OF ITS COMPLEXES WITH Ni(II), Co(II), Cu(II) AND UO₂(VI) METALS

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In this study, 1,2-dihydroxyimino-3,7-di-aza-9,10-O-iso-propylidene decane (**LH₂**) was synthesized starting from 1,2-O-iso-propylidene-4-aza-7-aminoheptane (**RNH₂**) and anti-chloroglyoxime. Complexes of this ligand with Ni(II), Co(II), Cu(II) and UO₂(VI) salts were prepared. Structures of the ligand and its complexes are proposed based on elemental analyses, IR, ¹³C and ¹H NMR spectra magnetic susceptibility measurements and thermogravimetric analyses (TGA).

Keywords: Vic-Dioxime; Nickel(II); Cobalt(II); Copper(II); Uranyl

INTRODUCTION

Recently, since the increasing use of coordination compound in analytical, biological, pigment and medical chemistry, many investigators have studied these topics, especially, the important role the complexes of vic-dioximes and their various derivatives have been a subject of study for a long period of time [1–8]. The transition metal complexes of vic-dioximes have been of particular interest as biological model compounds [1–9]. The substitution pattern of the vic-dioxime moiety affects the structure and stability of the complexes [5]. The presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms make vic-dioximes amphoteric ligands which form corrin-type square-planar [10], square pyramidal and octahedral complexes with transition metal ions such as Ni(II), Pd(II), Co(II) and Cu(II) as central atoms [11–17]. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar and octahedral structures which are stabilized by hydrogen bonding [18]. In the present paper, as part of our study to determine the coordination properties of various dioximes towards transition metal ions, we have synthesized four new complexes of 1,2-dihydroxyimino-3,7-di-aza-9,10-O-iso-propylidene decane, Reaction (3) with Ni(II), Co(II), Cu(II) and UO₂(VI). As far as we know, this is the first report of this ligand.

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EXPERIMENTAL

The preparation of anti-chloroglyoxime has been described previously [19]. All the reagents used were purchased from Merck or Fluka or Sigma Company and are chemically pure.

Elemental analyses were determined in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey), IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets, ^{13}C and ^1H NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR Spectrometer and a Jeol FX 90 Q FT-NMR. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20°C) using $\text{Hg}[\text{Co}(\text{SCN}_2)]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [20]. TGA curves were recorded on Shimadzu TG-50 thermobalance.

Synthesis of 1-chloro-2,3-O-iso-propylidene Propane (1)

15–20 drops of Borontrifluoride etherate, were added dropwise to 58 g (1.0 mole) of purified acetone. Then 23.0 g (0.25 mole) of epichlorohydrin was added dropwise to the mixture at $15\text{--}20^\circ\text{C}$ while stirring. After addition of epichlorohydrin, the reaction mixture was further stirred for 3 h at 20°C . The liquid product was distilled at $64\text{--}70^\circ\text{C}$ and 27 mm-Hg. Characteristic IR bands (NaCl cell, cm^{-1}) and ^1H NMR bands ($\text{DMSO-}d_6$, δ ppm) are in Tables II and V. Characteristic ^{13}C NMR bands ($\text{DMSO-}d_6$, δ ppm, 90 MHz): 27.20(C_1), 25.70(C_2), 110.00(C_3), 62.30(C_4), 70.00(C_5), 41.00(C_6).

Synthesis of 1,2-O-iso-propylidene-4-aza-7-aminoheptane (2)

In a reaction flask, a CaCl_2 drying tube and a dropping funnel, 16.70 mL (0.2 mole) of 1,3-diamino propane, 6.93 mL (0.05 mole) of triethylamine and 60 mL of absolute xylene were mixed and heated to 80°C . To this mixture, a solution of 7.5 g (0.05 mole) of 1-chloro-2,3-O-iso-propylidene propane (1) in 30 mL xylene was added dropwise, refluxed for 40 h and cooled to room temperature. The mixture was filtered and the filtrate was evaporated to remove the excess 1,3-diamino propane. The compound was distilled at $100\text{--}110^\circ\text{C}$ at 4 mm-Hg. Characteristic IR bands (NaCl cell, cm^{-1}) and ^1H NMR bands ($\text{DMSO-}d_6$, δ ppm) are in Tables II and V. Characteristic ^{13}C NMR resonances ($\text{DMSO-}d_6$, δ ppm) include: 26.68(C_1), 25.44(C_2), 108.98(C_3), 62.73(C_4), 70.56(C_5), 48.39(C_6), 38.34(C_7), 28.90(C_8), 35.60(C_9).

Synthesis of the ligand LH_2 (3)

A solution of NaHCO_3 (3.36 g, 0.04 mole) was added to a solution of 1,2-O-iso-propylidene-4-aza-7-aminoheptane (3.77 g, 0.02 mole) in 40 mL absolute ethanol, then a solution of anti-chloroglyoxime (2.45 g, 0.02 mole) in 30 mL absolute ethanol, which is synthesized by the method described previously [19], was added dropwise to the mixture at room temperature over 2 h; the mixture was stirred on a water bath at $60\text{--}70^\circ\text{C}$ for 10 h. The mixture was filtered and excess ethanol was removed by evaporation. The product was crystallized by addition of diethyl ether. Product was filtered off, washed

with diethyl ether and water several times and dried *in vacuo* for 24 h. The purified ligand (**LH₂**) is soluble in solvents such as C₂H₅OH, CHCl₃, DMSO and DMF. Characteristic IR bands (NaCl cell, cm⁻¹) and characteristic ¹H NMR peaks (DMSO-*d*₆, δ ppm) are shown in Tables II and V. Characteristic ¹³C NMR resonances (DMSO-*d*₆, δ ppm): 26.95(C₁), 25.80(C₂), 107.90(C₃), 62.00(C₄), 70.12(C₅), 48.30(C₆), 41.70(C₇), 32.10(C₈), 37.56(C₉), 146.00(C₁₀), 155.20(C₁₁).

Synthesis of Ni(II), Co(II) and Cu(II) Complexes

The ligand 0.549 g (0.002 mole) was dissolved in 10 mL absolute ethanol. A solution of 0.001 mole of metal salts [NiCl₂·6H₂O (0.238 g), CuCl₂·2H₂O (0.170 g), and CoCl₂·6H₂O (0.238 g)] in 10 mL absolute ethanol was added dropwise with continuous stirring. The apparent pH of the solutions, 5.0–5.5 by the addition of a 1% triethylamine solution in ethanol.

Every mixture was stirred 2 h more at 35°C, and the complexes thus precipitated were kept on a water bath for 30 min at 40°C, filtered and the precipitate washed with diethyl ether and water. The precipitate was dissolved in ethanol and the complexes were precipitated by addition of 25 mL diethyl ether. The crystals obtained were filtered, washed with diethyl ether and dried *in vacuo* at 60°C. The complexes are soluble in common solvents such as THF, DMF and DMSO.

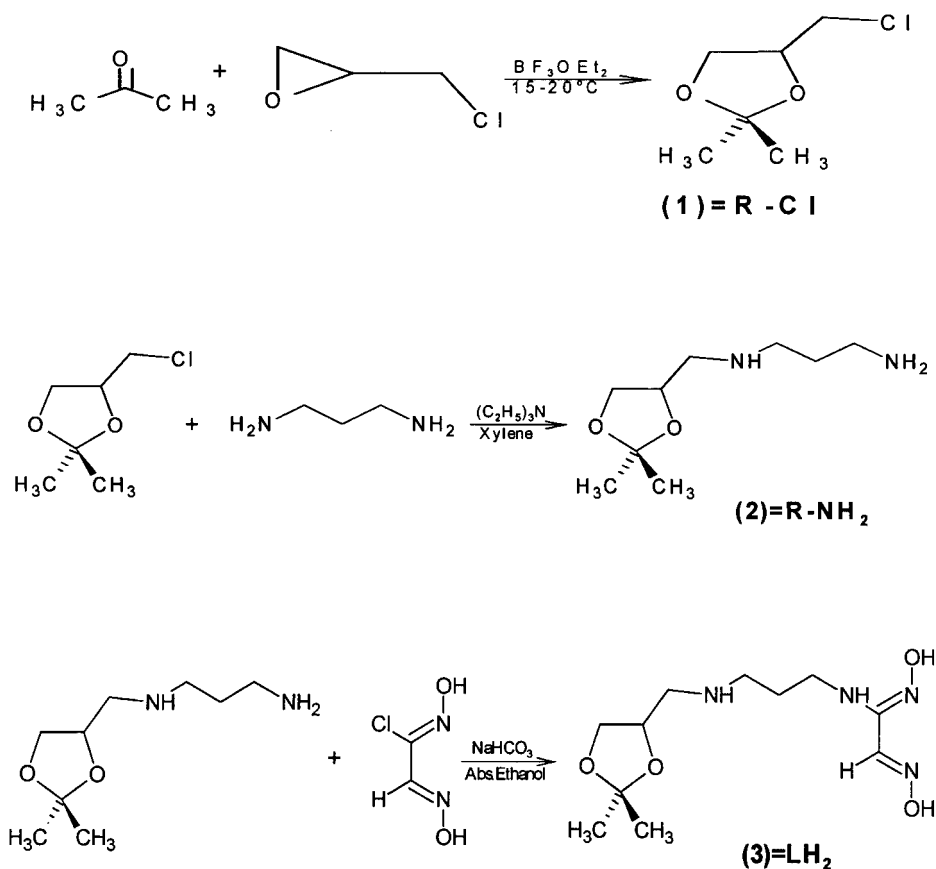
The Preparation of Uranyl Complex

To a solution of 0.274 g (0.001 mole) of **LH₂** in 20 mL absolute ethanol, a solution of 0.424 g (0.001 mole) of UO₂(CH₃COO)₂·2H₂O in 10 mL absolute ethanol was added. The orange complex which formed immediately was kept on a water bath for 10 min and filtered, washed with diethyl ether, water and ethanol. The crystals were dissolved in 20 mL of CHCl₃ and 100 mL of *n*-hexane was added to precipitate the compound. The crystals obtained were filtered, washed with diethyl ether and dried *in vacuo* at 60°C.

RESULTS AND DISCUSSION

The new ligand, 1,2-dihydroxyimino-3,7-di-aza-9,10-O-iso-propylidene decane (**LH₂**) was prepared in a three-stage process as shown in Scheme 1. The structural characterization data of (**1**) and (**2**) are given in the experimental section and Tables I, II and V. The structure of **LH₂** was determined by a combination of elemental analysis, IR, ¹H and ¹³C NMR spectroscopic techniques (Fig. 1).

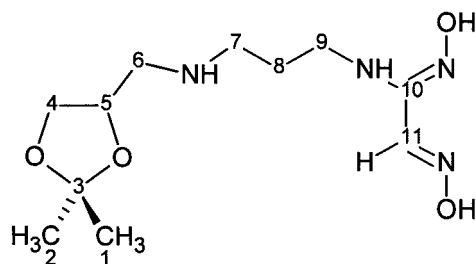
In the IR spectrum of (**2**), the characteristic bands are at 3412 cm⁻¹, which are assigned to ν(N–H) and ν(N–H₂) groups, respectively and at 1089 cm⁻¹, assigned to the ν(C–O–C) groups. There is no C–Cl band in the IR spectrum of (**2**). In the ¹H NMR spectra of (**2**), a peak appears at 2.76 ppm for (N–CH₂–) and 1.35 ppm for (–NH– and –NH₂) as broad peak. These peaks (–NH– and –NH₂) disappeared upon the addition of D₂O. Observation of the (–O–CH₂–) peaks at 3.55 and 3.80 ppm, as multiplets in each case, indicates that the compound undergoes *cis-trans* isomerization [16,21,22] Table V. The isomer ratios were found to be 52% *cis* and 48% *trans* from the ¹H NMR and ¹³C NMR data.



SCHEME 1

TABLE I The colors, formulas, formula weights, melting points, magnetic susceptibilities and yields of the ligand and the complexes

Compounds	<i>F.W</i> (g/mol)	Color	<i>M.P.</i> (dec) ($^\circ\text{C}$)	Yield %	μ_{eff} (B.M.)
R-Cl (1)					
$\text{C}_6\text{H}_{11}\text{O}_2\text{Cl}$	150.61	Colorless		71	—
R-NH ₂ (2)					
$\text{C}_9\text{H}_{19}\text{N}_2\text{O}_2$	188.10	Colorless		65	—
LH ₂ (3)					
$\text{C}_{11}\text{H}_{22}\text{N}_4\text{O}_4$	274.32	Dirtywhite	113	64	—
$\text{Ni}(\text{LH}_2)$					
$\text{C}_{22}\text{H}_{42}\text{N}_8\text{O}_8\text{Ni}$	605.31	Red	198	66	dia
$\text{Co}(\text{LH}_2) \cdot 2\text{H}_2\text{O}$					
$\text{C}_{22}\text{H}_{46}\text{N}_8\text{O}_{10}\text{Co}$	641.57	Darkbrown	176	55	4.61
$\text{Cu}(\text{LH}_2)$					
$\text{C}_{22}\text{H}_{42}\text{N}_8\text{O}_8\text{Cu}$	610.17	Darkgreen	143	59	1.64
$(\text{UO}_2)_2(\text{LH}_2)(\text{OH})_2$					
$\text{C}_{22}\text{H}_{44}\text{N}_8\text{O}_{14}\text{U}_2$	1120.69	Orange	225	61	dia

FIGURE 1 The structure of the ligand LH_2 .

The characterization of the ligand LH_2 was carried out by elemental analyses, IR, ^1H and ^{13}C NMR thermogravimetric analyses (TGA). In the IR spectrum of LH_2 , characteristic peaks appear at 3361 cm^{-1} $\nu(\text{N-H})$, 3280 cm^{-1} $\nu(\text{O-H})$, 1651 cm^{-1} $\nu(\text{C=N})$, 1089 cm^{-1} $\nu(\text{C-O-C})$ and 987 cm^{-1} $\nu(\text{N-O})$ as expected for a substituted vic-dioxime [23]. 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 [6,23]. In the LH_2 chemical shifts of $=\text{N-OH}$ protons were observed at 10.80 and 8.30 ppm as singlets. Also, chemical shifts of N-H protons were observed at 7.33 and 5.75 ppm. These bands are easily identified by deuterium exchange.

The C-H protons adjacent to the oxime groups were observed at about 7.82 ppm. This value is in agreement with the reported [5,24]. In the ^{13}C NMR, carbon resonances of dioxime groups (C_{10} and C_{11}) were observed at 146.00 and 155.20 ppm as expected for (E,E) dioxime [11,25]. The most characteristic signal for C_3 (ipso), is at 107.90 ppm.

The ligand LH_2 , 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 LH_2 indicates that the ligand is in the (E,E) form [26], the anti form of the ligand.

The mononuclear complexes of LH_2 with Ni(II), Co(II) and Cu(II) have a metal:ligand ratio of 1:2, but the Co(II) complex has two coordinated water molecules, in addition to the two ligand molecules. The infrared band observed near 1651 cm^{-1} , assigned to the $\nu(\text{C=N})$ frequency in the free ligand, is shifted to lower frequencies after complexation [3,27,29]. Meanwhile, the band observed at 987 cm^{-1} in the free ligand, assigned to the $\nu(\text{N-O})$, is shifted to lower frequency after complexation (Table II). For $\text{Co}(\text{LH}_2)_2 \cdot 2\text{H}_2\text{O}$, coordinated H_2O molecules are identified by a broad OH absorption around $3310\text{--}3500\text{ cm}^{-1}$. On the other hand, a band not seen in the free ligand which is assigned to $(\text{O} \cdots \text{H-O})$ [28,29] is observed at 1727 cm^{-1} for Ni(II), 1715 cm^{-1} for Co(II) and 1705 cm^{-1} for Cu(II). The absorptions indicate that the oxime group takes part in complexation.

The Co(II) and Cu(II) complexes are paramagnetic, whereas the Ni(II) complex is diamagnetic, and their magnetic susceptibility values are 4.61 and 1.64 B.M., respectively. For all these complexes, additional analytical data are given in Tables I-V. According to the above results, a square-planar geometry for Ni(II) and Cu(II) complexes and octahedral geometry for the Co(II) complex are proposed [30,31]. The suggested structures of the complexes are shown in Fig. 2. The Co(II) complex was characterized by IR, TGA and elemental analysis and two moles of water are

TABLE II Characteristic IR bands (cm^{-1}) of the ligand and complexes as KBr pellets

Compounds	O-H	N-H	Aliph C-H	N-O	C=N	Others
R-Cl	-	-	2902-3004	-	-	757 (C-Cl)
R-NH ₂	-	3412	2876-3004	-	-	1089 (C-O-C)
LH ₂	3280	3361	2902-3004	987	1651	-
Ni(LH) ₂	-	3348	2953-2978	972	1620	1727 (O...H-O)
Co(LH) ₂ · 2H ₂ O	3310-3500	3296	2876-2978	966	1630	3310-3554 (H ₂ O)
Cu(LH) ₂	-	3338	2953-2978	954	1610	1705 (O...H-O)
(UO ₂) ₂ (LH) ₂ (OH) ₂	3285-3517	3361	2953-3004	971	1590	920 (O-U=O)

TABLE III TGA data of the ligand and the complex

Compounds	Stability	I.Step	II.Step	Weight loss %	Residue
LH ₂	20-108	108-440	493-610	90	-
Ni(LH) ₂	20-189	189-400	420-582	87	NiO
Co(LH) ₂ · 2H ₂ O	20-165	165-340	405-620	92	Co ₃ O ₄
Cu(LH) ₂	20-158	158-299	302-746	85	CuO
(UO ₂) ₂ (LH) ₂ (OH) ₂	20-153	153-468	543-589	58	U ₃ O ₈

TABLE IV Elemental analyses of the ligand and the complexes

Compounds	Elemental analysis % calculated (found)		
	C	H	N
LH ₂	48.16(47.89)	8.08(8.50)	20.43(20.91)
Ni(LH) ₂	43.65(43.13)	6.99(6.51)	18.51(19.03)
Co(LH) ₂ · 2H ₂ O	41.19(41.62)	7.23(7.60)	17.46(17.72)
Cu(LH) ₂	43.31(43.76)	6.94(6.51)	18.36(18.79)
(UO ₂) ₂ (LH) ₂ (OH) ₂	23.58(23.94)	3.96(4.38)	10.00(10.46)

coordinated to the complex. Observation of O...H-O bond, leads us to consider the geometry of the complex to be octahedral [29].

The uranyl complex exhibits a different structure. The elemental analysis of the complex indicates that the metal : ligand ratio is 1 : 1. Uranyl complexes of vic-dioximes with this metal : ligand ratio are uncommon although we have reported a binuclear complex with μ -hydroxo bridges [3]. In the IR spectrum, the UO₂(VI) complex shows a band at 920 cm^{-1} which is assigned to $\nu(\text{O}=\text{U}=\text{O})$ [31] and there is not a O...H-O band. The band observed at 920 cm^{-1} is characteristic for (O=U=O) stretches and OH stretching vibrations of the oxime group still appear at 3285-3517 cm^{-1} as a broad band. These spectral data indicate a binuclear μ -hydroxo bridged non-planar structure for the uranyl diamagnetic complex **LH₂** [3]. The ¹H NMR spectrum of the uranyl complex shows two chemical shifts for the deuterium exchangeable N-OH (10.83 and 10.25 ppm) and -NH protons (6.74 and 5.79 ppm) (Table V). The suggested structure of the complex is shown in Fig. 3. Also this suggested structure is very suitable with the literature [3,31,32].

TGA data of **LH₂** and its metal complexes of Ni(II), Cu(II), Co(II) and UO₂(VI) are given in Table III. The decomposition temperature and the weight losses of the complexes were calculated from the TGA data. The ligand **LH₂** is stable up to 108°C

TABLE V ^1H NMR spectra of the ligand and the complexes in DMSO-d_6 in $\delta(\text{ppm})$

Compounds	$R\text{-Cl}$	$R\text{-NH}_2$	LH_2	$Ni(LH_2)_2$	$(UO_2)_2(LH_2)_2(OH)_2$
$N\text{-H}^a$	–	1.35 (3H) ^a	5.75–7.33 (2H) ^s	5.60 (4H) ^s	5.79–6.74 (4H) ^s
$N\text{-CH}_2^*$	–	2.76 (6H) ^m	3.00–3.40 (6H) ^m	3.41–3.44 (12H) ^m	3.36–3.90 (12H) ^m
$\text{-CH}_2\text{-}$	–	1.56 (2H) ^m	1.80–2.00 (2H) ^s	2.10–2.30 (4H) ^s	2.09–2.40 (4H) ^m
CH_3	1.40–1.50 (6H) ^s	1.45 (6H) ^s	1.33–1.40 (6H) ^s	1.30–1.42 (12H) ^s	1.31–1.39 (12H) ^s
-CH-O	4.00–4.10 (1H) ^m	3.90–4.00 (1H) ^m	4.10–4.50 (1H) ^m	4.20–4.40 (2H) ^m	4.25–4.50 (2H) ^m
$\text{-CH}_2\text{-O}$	3.40–3.70 (2H) ^m	3.55–3.80 (2H) ^m	3.35–3.70 (2H) ^m	3.40–4.30 (4H) ^m	3.50–4.40 (4H) ^m
$N\text{-OH}^{a,*}$	–	–	8.30–10.80 (2H) ^s	–	10.25–10.83 (2H) ^s
Others	3.80–4.00 (2H) ^m ($\text{CH}_2\text{-Cl}$)	–	7.82 (1H) ^s (H-C=N)	16.90 (2H) ^s ($\text{O-H}\cdots\text{O}$) ^a	

^mmultiplet; ^ssinglet; ^{*}broad bands; ^adeuterium exchangeable.

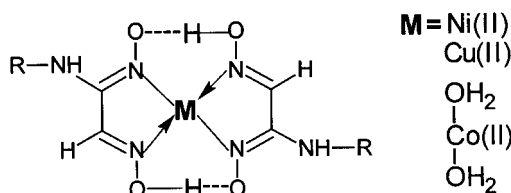


FIGURE 2 Suggested structure of the square-planar and octahedral complexes of the ligand LH_2 .

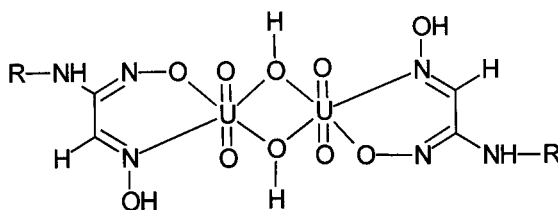


FIGURE 3 Suggested structure of the uranyl complex of the ligand LH_2 .

and its decomposition starts at 108°C and is completed at 610°C . As can be seen in the TGA data (Table III) all the complexes and the ligand decompose in two steps at different temperature ranges. All these complexes undergo complete decomposition to the corresponding metal oxides, NiO , CuO , Co_3O_4 or U_3O_8 .

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