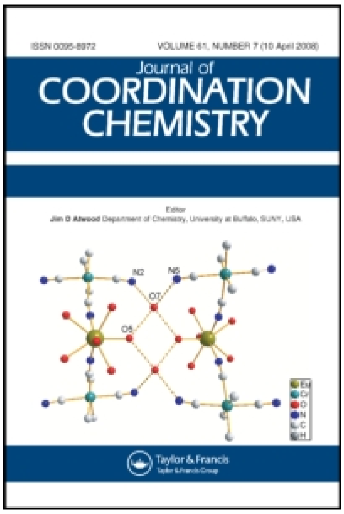

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SYNTHESIS OF 1,2-DIHYDROXYIMINO-l-PHENYL-3,7-DIAZA-9,10-O-BENZALOCTANE AND ITS COMPLEXES WITH Co(II), Cu(II) AND Ni(II)

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SYNTHESIS OF 1,2-DIHYDROXYIMINO-1-PHENYL-3,7-DIAZA-9,10-O-BENZALOCTANE AND ITS COMPLEXES WITH Co(II), Cu(II) AND Ni(II)

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A novel dioxime, 1,2 dihydroxyimino-3,7-diaza-9,10-O-benzaloctane (LH_2) was prepared by reaction of 1,2-O-benzylidene-4-aza-7-aminoheptane and *anti*-phenylchloroglyoxime in absolute ethanol. Mononuclear complexes with a metal–ligand ratio of 1 : 2 were prepared with Co(II), Cu(II) and Ni(II). To elucidate the structures of the ligand and complexes, elemental analyses, IR, ^1H NMR and ^{13}C NMR spectral data and magnetic susceptibility measurements have been examined.

Keywords: Dioxime; cobalt(II); copper(II); nickel(II); diaza macrocycle

INTRODUCTION

Numerous dioximes and their transition metal complexes have been investigated.[1] The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure which is stabilized by hydrogen bonding.[2] The high stability of the complexes with *vic*-dioxime ligands has been used extensively for various purposes. *vic*-Dioximes also have received considerable attention as model compounds which mimic biofunctions such as the reduction of vitamin B_{12}.[3,4] Compounds containing

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* Corresponding author.

the 1,3-dioxolane group are used as solvents, additives and as corrosion retardants. Polymers containing the 1,3-dioxolane group exhibit semiconducting behavior, while some polymers and copolymers of 1,3-dioxolane exhibit herbicidic and perfume activity.[5,6]

Gök has synthesized several ligands containing four aza or diaza-dithia groups and shown their capability of forming trinuclear complexes.[7] Gök *et al.* also have synthesized less aza compounds attached to the dioxime group.[8] Several similar compounds were synthesized by Gürol *et al.*,[9] Ahsen *et al.*[10] and Gök.[11] Sevindir has synthesized similar compounds and used them to complex some transition elements.[12] In all the articles mentioned above, similar complexation characteristics were observed as the ligand formed mononuclear complexes that contain unsaturated sites.

The aim of the present study was to synthesize and characterize a new dioxime containing a diaza macrocycle and to obtain its mononuclear complexes with Co(II), Cu(II), and Ni(II). Herein we report the synthesis of a new dioxime ligand containing long alkyl chains which are attached to oxolane groups.

EXPERIMENTAL

Reagents used in this work were of analytical grade. Benzaldehyde and epichlorohydrin were purchased from Merck (pure) and used without further purification. *Anti*-phenylchloroglyoxime was synthesized as described in the literature.[13]

The elemental analyses were determined in the TUBITAK Laboratory (Center of Sciences and Technology Research of Turkey), IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets, ^{13}C and ^{1}H NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR Spectrometer and a JEOL FX 90Q FT-NMR. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20°C) using $Hg[Co(SCN)_2]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants.[14] The refractive index of the substances was determined on a Bellingam + Stanley Ltd. 60/70 Abbe (calibration oil $RI = 1.47577$ at 20°C) refractometer. The metal contents of the complexes were determined by an Ati Unicam (Model 929) atomic absorption spectrophotometer in solutions prepared by decomposing the compounds in concentrated HCl and subsequent dilution with 0.01 M HCl.

Synthesis of 1-chloro-2,3-O-benzalpropane (1)

This substance was synthesized according to the method described in the literature,[15] with some modifications. The method was applied as follows: 15–20 drops of boron trifloride etherate were added dropwise to 106.0 g (1.0 mol) benzaldehyde. Then 28 g (0.30 mol) of epichlorohydrin was added dropwise to the reaction mixture at 10–20°C with continuous stirring. The reaction mixture was then further stirred for 3 h at 20°C. The product obtained was distilled at 130–133°C and 4 mmHg in *vacuum*; yield: 40 g (66%). The density of the product was found to be $d_4^{20} = 1.2169$. Elemental analysis for $C_{10}H_{11}O_2Cl$, calculated (found): C: 66.40 (66.20), H: 5.58 (5.66). Characteristic IR bands (NaCl cell, cm^{-1}): 2953–2876 (aliphatic C–H), 3055–3080 (aromatic C–H), 1095 υ(C–O–C), 745 υ(C–Cl). Characteristic ^1H NMR bands (CCl_4, TMS, δ ppm): 7.27 (5H, aromatic), 5.70 and 5.87 (1H, –CH <), 4.20 (1H, C–CH–O), 4.10 (2H, –O–CH_2–C), 3.50 (2H, –CH_2–Cl). Characteristic ^{13}C NMR bands (CCl_4, TMS, δ ppm): C_1(128.66), C_2(126.20 and 126.50), C_3(129.27 and 129.58), C_4(138.20 and 138.51), C_5(104.65 and 105.87), C_6(69.56 and 70.18), C_7(76.64 and 76.95), C_8(45.24 and 45.55).

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

29.6 mL (350 mmol) of 1,3-diamino propane, 10.0 mL (72 mmol) triethylamine and 100 mL absolute xylene were mixed in a reaction vessel and the temperature raised to 90°C with continuous stirring. To this solution, a solution of 14.3 g (72 mmol) of (**1**) in 50 mL absolute xylene was added dropwise. The mixture was further refluxed for 38 h. After cooling to room temperature the mixture was filtered and the filtrate distilled at 140–145°C at 2 mm Hg, yield: 13.0 g (76%). The density and the refractive index of the product were found to be $d_4^{20} = 1.0837$ and $n_D^{20} = 1.5398$, respectively. Elemental analysis, calculated (found) % for $C_{13}H_{20}N_2O_2$, C: 66.10 (66.35), H: 8.47 (8.50), N: 11.86 (11.58). Characteristic IR bands (NaCl cell, cm^{-1}): 3285–3361 υ(–NH, –NH_2), 2953–2876 υ(C–H), 1095 υ(C–O–C). Characteristic ^1H NMR bands ($CDCl_3$, TMS, δ ppm) are in Table III. Characteristic ^{13}C NMR bands ($CDCl_3$, TMS, δ ppm): C_1(131.20), C_2(131.78 and 132.0), C_3(129.44 and 129.73), C_4(134.7 and 135.3), C_5(107.18 and 108.06), C_6(75.09 and 74.97), C_7(82.50 and 82.08), C_8(54.17), C_9(59.15), C_{10}(40.01), C_{11}(58.57).

Synthesis of the Ligand LH_2 (3)

1.500 g (6.355 mmol) of 1,2-O-benzal-4-aza-7-aminoheptane in 15 mL absolute ethanol and 0.61 g (6.04 mmol) of triethylamine in 30 mL were mixed.

The mixture was cooled to –10°C and kept at this temperature, and a solution of 1.20 g (6.04 mmol) of *anti*-phenylchloroglyoxime in 50 mL absolute ethanol was added dropwise over a one hour period with continuous stirring. The mixture was further stirred for 30 min at this temperature and the precipitate was filtered. To obtain a high purity compound, the precipitate was recrystallized from an ethanol : water mixture (1 : 2) and dried in *vacuo* at 25°C. Yield: 1.73 g (59%), m.p. 58°C. The product is soluble in common solvents such as $CHCl_3$, C_2H_5OH, THF or DMSO.

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

A quantity of 0.300 g (0.753 mmol) of the ligand was dissolved in 15 mL absolute ethanol and a solution of 0.376 mmol of metal salt [$CoCl_2 \cdot 6H_2O$ (0.090 g), $CuCl_2 \cdot 2H_2O$ (0.064 g) and $NiCl_2 \cdot 6H_2O$ (0.0896 g)] in 5 mL absolute ethanol was added with continuous stirring. Different colored solutions were obtained as pH decreased from 9.8 to 4.0–4.5 stirring at 6°C on a water bath for 1 h. After cooling to room temperature, the complexes were filtered, washed with water, diethyl ether and ethanol and dried at 110°C for 24 h.

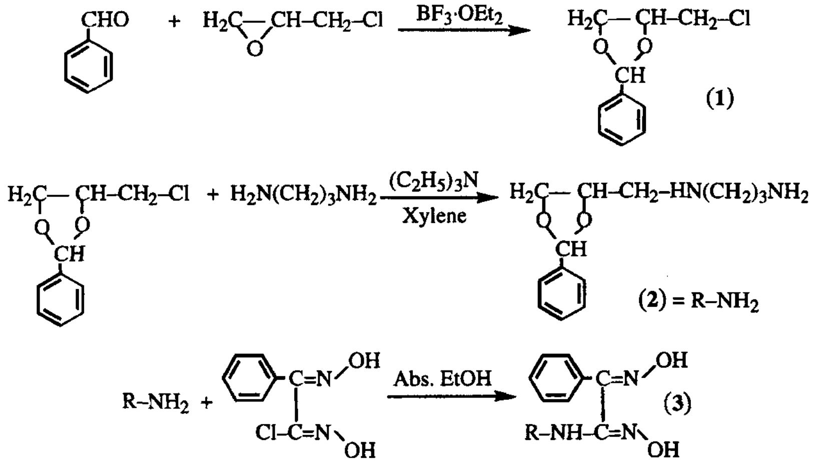
RESULTS AND DISCUSSION

The reaction steps for the synthesis of LH_2 are given in Scheme 1. The first step is synthesis of 1-chloro-2,3-O-benzal propane (**1**) from the reaction of benzaldehyde and epichlorohydrin. In this reaction $BF_3 \cdot OEt_2$ was used as catalyst. In the second step, 1-chloro-2,3-O-benzal propane and 1,3-diamino propane were reacted to obtain 1,2-O-benzal-4-aza-7-aminoheptane (**2**) (abbreviated as R-NH_2). In the third step, 1,2-hydroxyimino-1-phenyl-3,7-diaza-9,10-O-benzaloctane was obtained from the reaction of *anti*-phenylchloroglyoxime, which was obtained from the procedure published previously,[13] and 1,2-O-benzal-4-aza-7-aminoheptane, Scheme 1.

For the structural characterization of (**1**)–(**3**), IR, ^1H NMR and ^{13}C NMR were used and the data are given in the experimental section. Additional analytical data are given in Tables I–III.

In the IR spectrum of (**1**) the most characteristic absorptions are at 1095 cm^{-1} (C–O–C) and 745 cm^{-1} υ(C–Cl); characteristic ^1H NMR peaks are given in the experimental section.

In the IR spectrum of (**2**), the characteristic peaks are at 3361–3285 cm^{-1} which are assigned to υ(N–H) and υ(–NH_2) and the peak at 1095 cm^{-1} is assigned to the υ(C–O–C) group. There is no C–Cl stretch in the IR



SCHEME 1

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

Compounds	*F.W.* (g/mol)	*Color*	*m.p.* (°C (dec.))	*Yield* (%)	μ_{eff} [B.M.]	*Elemental analyses % calculated (found)* *C*	*H*	*N*
Ligand, LH_2 (**3**)	398.5	Grey	58	59	—	63.30	6.58	14.06
$C_{21}H_{26}N_4O_4$						(63.07)	(6.42)	(13.93)
$Co(LH)_2 \cdot 2H_2O$	889.9	Light Brown	201	67	3.57	56.69	6.12	12.59
$C_{42}H_{54}N_8O_{10}Co$						(56.42)	(6.21)	(12.82)
$Cu(LH)_2$	858.5	Black	174	58	1.76	58.76	5.83	13.05
$C_{42}H_{50}N_8O_8Cu$						(58.70)	(5.87)	(13.12)
$Ni(LH)_2$	853.6	Red	254	78	Dia	59.10	5.90	13.13
$C_{42}H_{50}N_8O_8Ni$						(58.88)	(5.55)	(12.80)

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

Compounds	*O–H*	*N–H*	*Aliph. C–H*	*O···H–O*	*C–O–C*	*N–O*	*C=N*
R–NH_2 (**2**)	—	3387	2953–2876	—	1094	—	—
LH_2 (**3**)	3285	3387	2953–2876	—	1094	989	1637, 1614
$Co(LH)_2 \cdot 2H_2O$	3200–3550	3382	2953–2876	1707, 1695	1094	932	1613, 1579
$Cu(LH)_2$	—	3387	2953–2876	1730, 1700	1094	966	1614, 1603
$Ni(LH)_2$	—	3387	2953–2876	1776, 1755	1094	920	1603, 1591

spectrum of (**2**). In the ^1H NMR spectra of (**2**), peaks appear at 2.4–3.2 ppm for (N–CH_2–) and at 1.75 ppm for (–NH–, and –NH_2) as a broad peak. These peaks (–NH–, and –NH_2) disappear with addition of D_2O. On the other hand, in the ^{13}C NMR spectrum of (**2**), each carbon, C_2, C_3, C_4, C_5,

TABLE III ^1H NMR spectra of the ligand and some complexes in DMSO-d_6 and $CDCl_3$ in δ (ppm)

Compound	*R–NH₂*	*LH₂*	*(LH)₂Ni*
OH^a	—	$11.50\,(1H)^s$, $10.98\,(1H)^s$	—
$(O\text{–}H\cdots O)^a$	—	—	$17.08\,(1H)^s$, $16.06\,(1H)^s$
$N\text{–}H^a$	$1.75\,(3H)^s$	$3.4\,(2H)^s$	$3.5\,(4H)^s$
φ–CH <	$5.60, 5.75\,(1H)^s$	$5.58, 5.65\,(1H)^d$	$6.26, 6.14\,(1H)^d$, $5.92, 5.85\,(1H)^d$
Ar–CH–	$7.42\,(5H)^m$	$8.2\text{–}6.7\,(10H)^m$	$7.8\text{–}7.0\,(20H)^m$
–CH–O–	$4.00\text{–}4.50\,(1H)^m$	$4.4\text{–}4.0\,(1H)^m$	$4.4\,(1H)^m$, $4.2\,(1H)^m$
$\text{–O–}CH_2\text{–C}$	$3.7\text{–}4.1\,(2H)^m$	$3.77\,(H)^m$, $3.3\,(1H)^m$	$4.1\,(2H)^m$, $3.9\,(2H)^m$
$N\text{–}CH_2$	$2.4\text{–}3.2\,(6H)^m$	$3.3\text{–}2.2\,(6H)^m$	$3.4\text{–}2.1\,(12H)^m$
$\text{–}CH_2\text{–}^{10}$	$2.08\,(2H)^m$	$1.15\text{–}1.80\,(2H)^m$	$1.26\,(2H)^m$, $1.43\,(2H)^m$

m: multiplet, s: singlet, d: doublet, a: deuterium exchangeable, φ–CH <: Oxolane. For Ref. 10 see Figure 1.

C_6 and C_7 has a double resonance which is (131.78 and 132.00), (129.44 and 129.73), (134.7 and 135.3), (107.18 and 108.06), and (75.09 and 74.97) ppm, respectively, indicating that compound (**2**) has a *cis-trans* isomerism.[16] The isomer ratio was found to be 56% *cis*-isomer and 44% *trans*-isomer from the ^1H NMR and ^{13}C NMR data.

In the ^1H NMR spectrum of LH_2, a singlet, the deuterium-exchangeable protons of the =N–OH groups appear at $\delta = 11.50$ and 10.98 ppm. When the chemical shift values of two OH groups in the ligand are compared, the peak at lower field varies little (11.50 ppm), while a considerable difference is observed for those at higher field (10.98 ppm). Consequently, since the effect of different substituents is expected to be higher on the amidoxime group, the first one is assigned to the OH proton adjacent to phenyl, and the second one to the OH protons of the amidoxime group. The multiplet at $\delta = 8.2\text{–}6.7$ ppm corresponding to aromatic protons are not significantly shifted compared with (**2**). The observed peak at $\delta = 3.4$ ppm for –NH protons disappears upon addition of D_2O. Additional ^1H NMR data are given in Table III. More detailed information about the structure of LH_2 is provided by the ^{13}C NMR spectra. The carbon resonances of the oxime groups appear at two different fields, $\delta = 156.5$ and 152.5 ppm. The other carbon resonances of this ligand are at $\delta = C_4(138.3$ and $138.1)$, $C_5(103.1$ and $104.1)$, $C_6(68.5$ and $67.9)$, $C_7(75.6$ and $74.0)$, $C_8(51.5$ and $49.7)$, $C_9(46.9$ and $46.3)$, $C_{10}(30.3$ and $29.9)$, $C_{11}(42.3$ and $40.6)$, $C_{12}(156.5)$, $C_{13}(152.5)$ ppm. Since the ligand has *cis-trans* isomerism, all the carbon atoms, except for C_{12} and C_{13}, have double resonances. On the other hand. C_1, C_2, C_3, C_{15}, C_{16} and C_{17} carbons have single resonances at 127.1, 127.3, 129.1, 129.2, 129.8 and 130.0 ppm, but since their environments are similar, which resonance belongs to which carbon atom has not been determined. In the ^1H NMR, φ–CH< and $\text{–O–}CH_2\text{–}$ groups have double resonances.

This shows that the ligand has *cis-trans* isomerism (Table III). The isomer ratio was found to be 60% *cis*-isomer and 40% *trans*-isomer from the ^1H NMR data.

The IR spectrum of the new compound LH_2, O–H shows stretching vibrations at 3285 cm^{-1}. The N–H, and N–O bands are found at 3387 and 978 cm^{-1}, respectively. Since their environments are different, two different C=N vibrations were observed at 1637 and 1614 cm^{-1}. Oxolane bridges (C–O–C) show their band at 1094 cm^{-1} as expected for the oxolane bearing molecules. According to the elemental analyses, IR, ^{13}C and ^1H NMR results, the structure of the ligand is consistent with that shown in Figure 1.

The mononuclear complexes of LH_2 with Co(II), Cu(II) and Ni(II) have metal : ligand ratio of 1 : 2. In all these complexes, a band not seen in the free ligand is assigned to $v(O\cdots H{-}O)$,[11,17] observed at 1707 and 1695 cm^{-1} for $Co(LH)_2 \cdot 2H_2O$, 1700 and 1730 cm^{-1} for $Cu(LH)_2$ and 1776 and 1755 cm^{-1} for $Ni(LH)_2$. Thus the oxime group takes part in complexation. The infrared bands observed near 1637 and 1614 cm^{-1} which are assigned to the $v(C{=}N)$ frequency in the free ligand, are shifted to lower frequencies after complexation (Table II). This shift of the C=N vibration to lower frequencies for all the complexes is due to N,N-metal chelation.[11,18] In the case of $Co(LH)_2 \cdot 2H_2O$ complex, the coordinated H_2O molecules are identified by broad OH absorptions around 3200–3550 cm^{-1} which retain their intensities even after heating at 110°C for 24 h. The ^1H NMR spectrum of the Ni(II) complex shows two bands at $\delta = 17.08$ and 16.06 ppm supporting the proposed $(O\cdots H{-}O)$ bridge[10,11] and this result can be easily identified by deuterium exchange. The Co(II) and Cu(II) complexes are paramagnetic, whereas the Ni(II) complex is diamagnetic, and their magnetic susceptibility values are 3.57 and 1.76 B.M., respectively. The alternative chemical environments will give two $(O\cdots H{-}O)$ bridge protons in the *cis*-form, but only one in the *trans*-form. Observation of the $(O\cdots H{-}O)$ in the IR spectrum and ^1H NMR spectra at two different frequencies in each case,

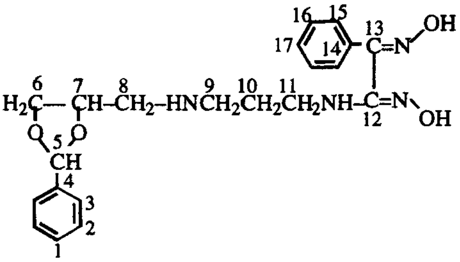


FIGURE 1 The structure of the ligand LH_2.

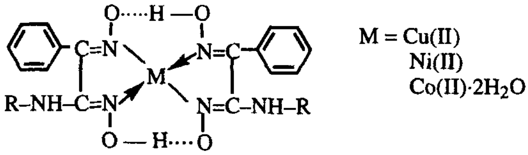


FIGURE 2 Suggested structure of the square-planar and octahedral complexes of the ligand LH_2.

indicate that the Ni(II) complex is in the *cis*-form. According to the above results, a square-planar geometry for the Ni(II) and Cu(II) complexes, and an octahedral geometry for the Co(II) complex are proposed.[19,20] The suggested structures of the complexes are shown in Figure 2.

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