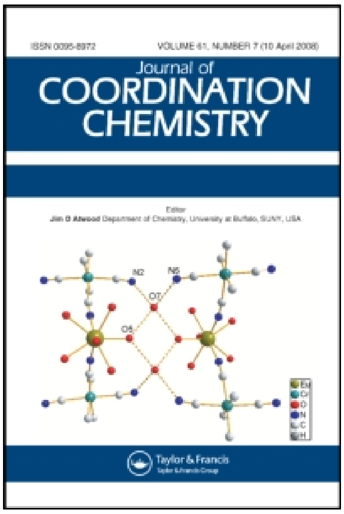

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SYNTHESIS OF A NEW GLYOXIME DERIVATIVE, CHARACTERIZATION AND INVESTIGATION OF ITS COMPLEXES WITH NI(II), CO(II), CU(II) AND UO$_2$(VI) METALS

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SYNTHESIS OF A NEW GLYOXIME DERIVATIVE, CHARACTERIZATION AND INVESTIGATION OF ITS COMPLEXES WITH NI(II), CO(II), CU(II) AND UO_2(VI) METALS

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In this study, a novel dioxime having the 1,3-oxolane group, 1,2-dihydroxyimino-3,7-di-aza-9,10-O-cyclohexylidene decane (H_2L), has been synthesized from the reaction of 1,2-O-cyclohexylidene-4-aza-7-amino heptane and *anti*-chloroglyoxime. Complexes of this ligand with Ni(II), Co(II), Cu(II) and UO_2(VI) salts were prepared. The structure of the ligand and its complexes is proposed from the ^{1}H and ^{13}C-NMR, IR, mass spectral data, elemental analysis and magnetic susceptibility measurements. In addition, thermal properties of H_2L and its complexes were also investigated by thermogravimetric analyses (TGA) and differential thermal analyses (DTA).

Keywords: dioxime; glyoxime; nickel(II); cobolt(II); copper(II)

INTRODUCTION

The transition metal complexes of *vic*-dioximes have been of particular interest as biological model compounds[1]. The transition metal complexes of *vic*-dioximes have been extensively investigated for their similarity with vitamin B_{12}.[2-4] Most of the work carried out has been on symmetrically disubstituted glyoximes and monosubstituted ones.[3,5] The presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms make *vic*-dioximes amphoteric ligands which form corrin-type square-planar,[6] square pyramidal and octahedral complexes with

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transition metal ions such as Cu(II) Ni(II), Pd(II), Co(II) and Cu(II) as central atoms.[7] 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.[8] In the present paper, as part of our study to determine the coordination and semiconductor 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-cyclohexylidene decane, Reaction (3) and Ni(II), Co(II), Cu(II) and UO_2(VI). As far as we know, this is the first report on this ligand.

EXPERIMENTAL

The preparation of *anti*-chloroglyoxime has been described previously.[9] Elemental analyses were performed in the TUBITAK laboratory (Center of Science and Technology Research Council of Turkey), IR and electronic spectra were recorded on a Mattson 1000 FT-IR and a SECOMAM 1000 spectrophotometer (1 cm quartz cells), respectively. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-200 FT-NMR. Mass spectrometry (MS) was also used in characterization of the ligand. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility (Model No: MK1) balance at room temperature using $Hg[Co(SCN)_4]$ as a calibrant. Thermal analysis data were obtained using a Shimatzu DTA-50 instrument and a TG-50 thermobalance.

Preparation of the Compounds

For the synthesis of 1-chloro-2,3-O-cyclohexylidene propane (**1**), 15-20 drops of boron trifluoride etherate, BF_3OEt_2, were added dropwise to 98 g (1000 mmole) of cyclohexanone. Then 23.0 g (250 mmole) of epichlorohydrine was added dropwise to the mixture at 10-17° C while it was stirred. After addition of epichlorohydrine, the reaction mixture was further stirred for 2 h at 20° C. The liquid product was distilled at 108-110° C and 13 mm Hg in *vacuum*. Yield: 38.1 g, (80%). Relative density of the product was found to be 1.1484, using a pycnometer, $n_D^{20} = 1.4772$. IR (NaCl cells, cm^{-1}): 2960 (C-H), 1105 ($O-CH_2-CH-O$), 745 (C-Cl). ^1H-NMR (CCl_4, TMS, δ, ppm): 1.52 [m, ($-CH_2$, in cyclo structure), 10H], 3.2-4.4 [m, (CH_2-Cl, $O-CH_2-CH-O$, 5H]. Analysis (found %): C: 56.80; H: 7.75. Calculated (%) for $C_9H_{15}ClO_2$: C: 56.69, H: 7.87.

1,2-O-Cyclohexylidene-4-aza-7-amino Heptane (2)

To a solution of 16.74 mL (200 mmole) 1,3-diaminopropane and 8 mL (57 mmole) triethylamine in 50 mL absolute xylene, a solution of 9.5 g (50 mmole) of compound (**1**) in 50 mL absolute xylene, was added dropwise. The addition of compound **1** was started at 80° C. The mixture was stirred and refluxed for 35 h. After cooling to room temperature, the mixture was filtered to separate the triethylamine salt formed. The product obtained was distilled at 137-143° C and 4 mm Hg. Yield: 7.2 g (63 %). Relative density of the product was found to be 1.0583, using a pycnometer. $n_D^{20}=1.4818$. IR (NaCl cells, cm^{-1}): 3350-3450 (-NH-, -NH_2), 2950-2740 (C-H), 1105 (O-CH_2-CH-O). Mass spectrum (EI): m/z = 229 $[M+1]^+$. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.48-1.54 [m, (CH_2 in cyclo structure) 10H], 1.58-1.65 [m, (CH_2), 2H], 1.65-1.68 [t, (-NH_2), 2H], 2.56-2.64 [m, (N-CH_2, -NH), 7H], 3.48-4.23 [m, (O-CH_2-CH-O), 3H]. ^{13}C NMR ($CDCl_3$, δ, ppm): 109.39; 75.47; 68.07; 53.44; 48.07; 40.48; 36.57; 36.45; 23.47; 22.90. Analysis: (found %): C: 62.85; H: 10.43; N: 11.80. Calculated (%) for $C_{12}H_{22}N_2O_2$: C: 63.10, H: 10.50, N: 12.2

1,2-Dihydoxyimino-3,7-di aza-9,10-O-Cyclohxylidene Decane (H_2L)

A solution of $NaHCO_3$ (3.51 g, 41 mmole) was added to a solution of 1,2-O-cyclohexylidene 4-aza-7- aminoheptane (4.56 g, 20 mmole) in 40 mL absolute ethanol, then a solution of *anti*-chloroglyoxime (2.45 g, 20 mmole) in 30 mL absolute ethanol, which is synthesized by the method described previously,[9] was added dropwise to the mixture at room temperature over 2 h, the mixture was stirred on a water bath at 60-70° C for 5 h more. The yellow mixture was filtered and excess ethanol was removed by evaporation. The product was crystallized by addition of diethyl ether. Obtained product was filtered off, washed with diethyl ether several times and dried in *vacuum* for 24 h. The purified ligand (H_2L) is soluble in common solvents such as C_2H_5OH, H_2O and $CHCl_3$.

^{1}H NMR (DMSO-d_6, δ): 9.07 (s, O-H, 1H), 8.57 (s, O-H, 1H), 7.86 (s, H-C=N, 1H), 6.49 (s, N-H, 1H), 6.22 (s, N-H, 1H), 4.36-3.08 (m, O-CH_2-CH-O, 3H), 1.60-1.40 [m, (CH_2- in cyclo structure), 10H]. ^{13}C-NMR (DMSO-d_6, δ, ppm): 154.35; 141.09; 110.98; 74.50; 67.47; 51.30; 46.13; 37.59; 35.50; 25.43; 24.47; 19.29. Mass spectrum (EI): m/z = 316 $[M+2]^+$ and 254 [M-2(NO)]. Analysis (found) % : C: 52.93; H: 7.89; N: 17.35. Calculated (%) for $C_{14}H_{26}N_4O_4$: C: 52.50; H: 8.28; N: 17.83.

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

A solution of 1 mmole metal salt, [$NiCl_2{\cdot}6H_2O$ (0.119 g), $(CH_3COO)_2Co{\cdot}4H_2O$ (0.248 g), $Cu(CH_3COO)_2{\cdot}H_2O$ (0.119 g)] in 20 mL distilled water were added to the solution of the ligand (2 mmole, 0.628 g) in 20 mL ethanol. The pH of the mixture was adjusted to 4.5-5.0 with addition of 0.100 N NaOH solution. Before

TABLE I The colors, yields, melting points, magnetic moments, and elemental analyses of the ligand and complexes.

Compounds	*Color*	*Yield* %	M.p.°C (dec.)	μ_{eff} (B.M)	*Elemental Analyses (found) %*		
					C	H	N
H_2L	Pale Yellow	60.3	115	-	53.55 (53.62)	8.28 (7.89)	17.83 (17.45)
$(HL)_2Ni$	Red	50.1	206	Dia	49.06 (49.41)	7.30 (7.66)	16.35 (16.11)
$(HL)_2Co{\cdot}2H_2O$	Brown	49.2	175	4.64	46.60 (46.83)	7.48 (7.50)	15.53 (15.17)
$(HL)_2Cu{\cdot}H_2O$	Dark Brown	51.0	145	1.63	47.49 (47.15)	7.34 (7.40)	15.82 (15.49)
$[(HL)UO_2(OH)]2{\cdot}2H_2O$	Orange Yellow	85.2	-	Dia	27.27 (27.38)	4.54 (4.19)	9.09 (8.73)

filtration, to complete precipitation, the mixture was kept on a water bath at 25° C for 2 h. The complexes formed were filtered off, washed with water, diethyl ether, cold ethanol and dried in *vacuum* at 70° C.

The Preparation of Uranyl Complex

A solution of 1 mmole (0.662 g) of uranyl salt $[(CH_2COO)_2UO_2{\cdot}2H_2O)]$ in 20 mL ethanol was added to a solution of ligand (1 mmole, 0.314 g) in 20 mL ethanol. The complex formed immediately, was filtered off, washed with water and diethyl ether and dried in vacuum at 50° C.

The colors, yields melting points, elemental analyses, characteristic IR bands, magnetic moments, UV-visible data, and TGA and DTA measurements for the ligand and the complexes are given in Tables I-III.

RESULTS AND DISCUSSION

In this study, a new *vic*-dioxime ligand which has donor groups of nitrogen and oxygen has been synthesized. 1-chloro-2,3-o-cyclohexylidenepropane (**1**) was

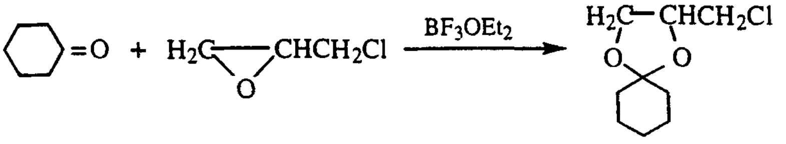
TABLE II Characteristic IR bands (cm^{-1}, as KBr pellet) of the ligand and the complexes.

Compounds	ν(N-H)	ν(O-H)	ν(C-H)	ν(O..H-O)	ν(C=N)	ν(N-O)	$\nu(H_2O)$
H_2L	3400	3285	2950-2740	-	1620	975	-
$(HL)_2Ni$	3400	-	2935-2865	1734	1590	975	-
$(HL)_2Co.2H_2O$	-	-	2945-2876	1760	1600	1000	3310-3580
$(HL)_2Cu.H_2O$	3383	-	2940-2860	1710	1600	955	3270-3100
$[HL)UO_2(OH)]2.2H_2O$	3365	3224-3550	2942-2871	-	1619	962	3300-3200

TABLE III Characteristic UV-VIS Bands and thermal analyses results of the ligand and the complexes.

Compounds	*UV λmax (nm), (DMF)*	*Decomposition Temperature °C*	*Weight Loss %*	*Residue*	*DTA Exo (°C)*	*Peaks Endo (°C)*
H_2L	291	122-510	97	-	102,486,511	-
$(HL)_2Ni$	315,375,484,660	182-460, 467-585	89	NiO	236, 458	
$(HL)_2Co{\cdot}2H_2O$	300,327,415	75-180, 182-350, 379-517	88	Co_3O_4	267,329,449	-
$(HL)_2Cu{\cdot}H_2O$	294,366	75-148, 148-349 466-606	87	CuO	175, 565	67, 388
$[HL)UO_2(OH)]2{\cdot}2H_2O$	312-352,414-570	60-114,164-458	51	U_3O_8	65,264,383	-

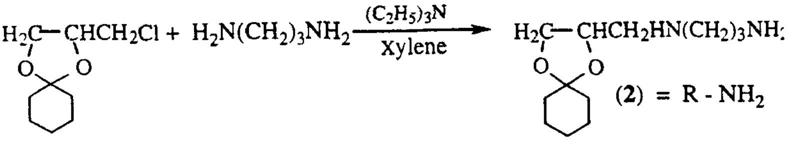
synthesized by the reaction of cyclohexanone and epichlorohydrine using BF_3 OEt_2 as a catalyst, Reaction **1**.



(1)

In the IR spectrum of compound (**1**), the characteristic C-H vibration band and the C-O-C asymmetric stretching vibration band are at 2950-2740 and 1105 cm^{-1}, respectively. The ^1H NMR spectra of compound (**1**) in CCl_4 shows two proton signals at 1.52 ppm [m, $-CH_2-$ in cyclo structure, 10H] and 3.2-4.4 ppm [m, (CH_2-Cl and O-CH_2-CH-O), 5H].

1,2-O-cyclohexylidene-4-aza-7-aminoheptane was synthesized by the reaction of 1-chloro-2,3-O-cyclohexylidenepropane and 1,3 propane diamine, Reaction 2.



(2)

The characteristic (-NH, $-NH_2$) bands in the IR spectrum of the compound (**2**) were observed at 3450 and 3350 cm^{-1}. In the ^1H NMR spectra, the $-NH_2$ and -NH- protons were observed at 1.65-1.68 ppm and 2.56-2.64 ppm, respectively; these signals disappear on addition of D_2O. Electron-Impact mass spectrometric data show a molecular ion peak m/z = 229 $(M+1)^+$ in agreement with the structure, presented in Figure 1. More detailed information about the structure of compound (**2**) is provided by the ^{13}C NMR spectra. The carbon resonances of this compound show ten chemical shifts in ppm: 23.47 (C_{10}), 22.90 (C_9), 36.57 (C_8),

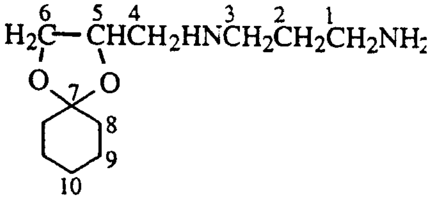
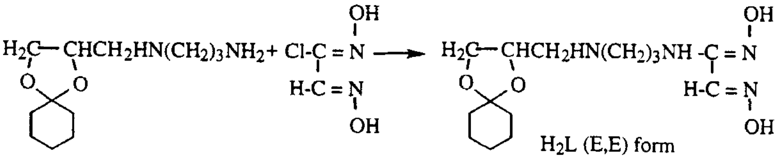


Figure 1. Structure of (**2**).

109.39 (C_7), 68.07 (C_6), 75.47 (C_5), 53.44 (C_4), 36.57 (C_3), 36.45 (C_2), and 40.43 (C_1). The most characteristic signal, for C_7 (ipso), is at 109.39 ppm.

According to the elemental analyses, mass, IR, ^{1}H and ^{13}C NMR spectral data, the proposed structure of the compound (**2**) is seen in Figure 1.

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.



(3)

The red color for the Ni (II) complex of H_2L indicates that the ligand is in the (*E,E*) form,[12] the *anti* form of the ligand.

The electron impact mass spectrum of H_2L, which shows a molecular ion peak at m/z: 316 $[M+2]^+$ and 254 confirms the proposed structure. The last parent ion shows the loss of m/z of 60 which can be explained by removal of 2(NO) from the molecule.[10] In the ^{1}H-NMR spectra, since the OH protons of the oxime groups are not equivalent, two peaks are observed for the protons.[11-13] In the H_2L, chemical shifts of =N-OH protons are observed at 9.07 and 8.57 ppm as singlets. Also, chemical shifts of N-H protons are observed at 6.49 and 6.22 ppm. These chemical shifts disappear upon addition of D_2O to the solution.

The C-H protons adjacent to the oxime groups were observed at about 8.30 ppm. This value is in agreement with the reported[13,14] values for oximes. In the ^{13}C NMR spectrum, the carbon resonances of oxime groups are observed at 154.35 and 141.09 ppm. In the IR spectrum of H_2L, -NH (3400 cm^{-1}), OH (3285 cm^{-1}), C=N (1620 cm^{-1}) and NO (975 cm^{-1}) stretching absorptions appear at frequencies as expected for the substituted aminoglyoximes,[5,14] Table II.

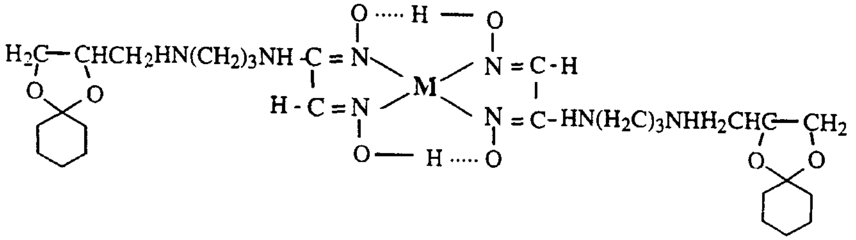


Figure 2. Octahedral and Square-Planar Complexes of the Ligand, H_2L. M = Ni(II), Cu(II), Co(II)·$2H_2O$

The IR spectra of the complexes, except for the uranyl complex, support the structures in Figure 2 by the weak bonding vibration of the H-O...H bridges around 1760-1710 cm^{-1} and the shift of the C=N vibration to lower frequencies 1600-1590 cm^{-1} due to N,N-metal coordination.[5,6] Magnetic susceptibility measurements provide sufficient data to characterize the structure of the complexes, Table I. The mononuclear complex of Ni (II) is diamagnetic as expected for a d^8 metal ion in a square-planar field.[5,15,16,7e] The magnetic moment of the mononuclear complex of Cu(II) is 1.63 B.M., comparable to the values reported for slightly distorted square planar Cu(II) complexes of *vic*-dioxime.[13,16]

The d^7 complex of Co(II) is paramagnetic and the magnetic susceptibility value is 4.64 B.M. The Co(II) complex was characterized by IR, TGA and elemental analysis and it was found that two moles of water are coordinated to the complex. Observation of O...H-O bond, leads us to consider the geometry of complex to be octahedral.[17] The UV-Vis spectrum of the complex supports this structure because $\pi-\pi^*$ and d-d transitions were observed, Table III.

The uranyl complex of H_2L was prepared from the acetate salt of the metal ion and the ligand in ethanol. 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.[7e] In the IR spectrum of the uranyl complex, the OH stretching vibrations of the oxime groups still appear as a broad band. A strong band around 914 cm^{-1} is the most characteristic frequency for O=U=O stretches.[18]

These spectral data lead us to a binuclear μ-hydroxo-bridged non-planar structure[7e,18-20] for the uranyl complex of H_2L, Figure 3. In the diamagnetic complex of UO_2(VI), the charge-transfer transitions were observed, Table III. TGA and DTA data of LH_2 and its metal complexes of Cu(II), Co(II) and UO_2 (VI) are given in Table III. The decomposition temperature and the weight losses

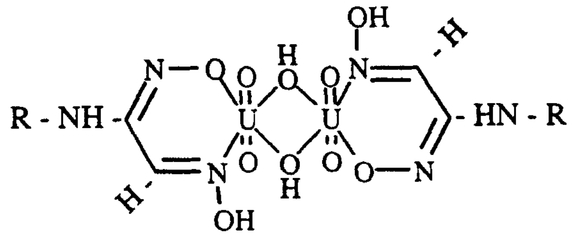


Figure 3. The structure of $(LH)UO_2(OH)_2UO_2(LH){\cdot}2H_2O$.

of the complexes were calculated from the TGA data. Exothermic and endothermic temperature values of the complexes were also obtained from the DTA data. Observed weight losses for the Cu(II), Co(II) and UO_2(VI) complexes from the TGA data are 2.56, 5.1, and 3.33 percent, respectively. This suggests that these complexes have 1, 2, and 2 mole water per complex molecule in the crystal structure, respectively. While Cu(II) and UO_2(VI) complexes were decomposed at low temperature, the decomposition of the Co(II) complex above 180° C suggests that the two moles of water are in the coordination sphere. This is also supported by the elemental analysis data.

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