SYNTHESIS OF THREE NEW VIC-DIOXIMES AND THEIR NICKEL(II) AND COPPER(II) COMPLEXES

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ABSTRACT

In this study, anti-1-acetyl-1-cyclohexenylchloroglyoxime ($C_8H_{11}ClN_2O_2$) has been synthesized by chlorination of anti-1-acetyl-1-cyclohexenylglyoxime. As a result of the reaction of $C_8H_{11}ClN_2O_2$ with aryl- or arylalkylamines in ethanol between $-10^\circ C$ and $-15^\circ C$, unsymmetrical vic-dioximes were obtained and the obtained products were named as: anilino-1-acetyl-1-cyclohexenylglyoxime ($C_{14}H_{17}N_3O_2$), benzylamino-1-acetyl-1-cyclohexenylglyoxime ($C_{15}H_{19}N_3O_2$), p-toluidino-1-acetyl-1-cyclohexenylglyoxime ($C_{15}H_{19}N_3O_2$) respectively. Their transition metal complexes have been synthesized. The form of the obtained Ni(II) and Cu(II) complexes were found as square-planar as it is known usually. 1H n.m.r., conductivity measurements, magnetic properties, i.r spectra and elemental analyses data of ligands and complexes are given. In addition to this, thermal characterizations of the ligands and their complexes have been investigated.

Key Words: Copper(II), Ligands, Nickel(II), Oximes, vic-dioximes,

INTRODUCTION

Vic-dioximes have received considerable attention as model compounds which mimic bifunctions such as the reduction of B_{12} ^{1,2}. Oxime metal chelates are biologically active³ and are reported to possess semiconduction properties^{4,5}. Derivates of some momoaminoglyoxime, vic-dioximes, tetraoximes and their transition metal complexes have been described^{2,6-16}.

Nowadays, vic-dioximes are appreciated as coordination compounds in lots of usage areas such as analytical, biologically, pigment and medicinal chemistry. Many researchers have studied vic-dioximes, and the important role of the complexes especially 1,2-dioximes in coordination chemistry^{4,5}. The substitution pattern of vic-dioxime moiety affects the structure and stability of the complexes⁴⁻⁸, but the complexes are decomposed in the case of aminoglyoxime derivatives¹⁷. In the present paper, I report the synthesis of and complex formation by two new substituted amino-1-acetyl-1-cyclohexenylglyoximes as examples of unsymmetrically substituted vic-dioximes. The unsymmetry of the ligands is also expected to enhance the solubility of planar complexes derived from them.

EXPERIMENTAL SECTION

Materials and methods

1-acetyl-1-cyclohexene was bought ready-made from Merck. Anti-1-acetyl-1-cyclohexenylglyoxime was prepared by reported procedures^{13,17-19}. M.p.s.'s were measured on an Electrothermal IA 9100 digital melting point apparatus. Elemental analyses (C, H and N) were realized using a Carlo-Erba 1106 model analyzer. 1H -n.m.r. and i.r. spectra were obtained with Bruker 200 MHz spectrometer and Jasco FT/Ir-300 instrument, respectively. The pH of the solutions were adjusted and controlled with WTW pH.537 pH meter. Molar conductance of the ligands and their metal complexes were determined at room temperature using a CMD 750 WPA conductivity meter. TGA curves were recorded on a Shimadzu TG-50 thermo balance.

Synthesis

Anti-1-acetyl-1-cyclohexenylchloroglyoximes, anti- $C_8H_{11}ClN_2O_2$

Dry chloro gas was passed through a suspension of anti-1-acetyl-1-cyclohexenylglyoxime (3.36 g, 0.020 mol) in 30 mL chloroform under sun light for $\frac{1}{2}$ h until the color of suspended material became grey. After the transition of Cl_2 for 2 h under UV-irradiation (254 nm), it was observed that the temperature of the mixture reached $35^\circ C$ and crystals formed. The mixture was cooled to room temperature, excess Cl_2 was expelled in vacuum and then the solution was filtered and the solid was washed with chloroform and then water. By the recrystallization in ethanol-water (1:2) 3.95 g (%78) product was gained with m.p. as $130^\circ C$.

It was determined that this obtained compound was soluble in ethanol, DMSO, DMF and diethyl ether but insoluble in water.

Synthesis of Substituted Amino-1-acetyl-1-cyclohexenylglyoximes [L^1H_2], [L^2H_2] and [L^3H_2]

The solution of 0.01 mol freshly distilled amino compounds such as [aniline (2 mL), benzylamine (2.2 mL), p-toluidine (1.07 g)] in absolute ethanol (30 mL) was added to a stirred of anti- $C_8H_{11}ClN_2O_2$ (2.025 g, 0.01 mol) in absolute ethanol (35 mL) between $-10^\circ C$ and $-15^\circ C$ drop by drop in 30 min. The reaction mixture was further stirred for 2 h and then diluted with water to 120 mL and left overnight at $5^\circ C$. The precipitate was filtered and then recrystallized from ethanol-water (1:2). The crystalline product was filtered, washed with water and dried at room temperature.

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

When a solution of 0.6 mmol metal salt [$NiCl_2 \cdot 6H_2O$ (0.143 g), $CuCl_2 \cdot 2H_2O$ (0.103 g)] in 25 mL absolute ethanol was added into a solution of the ligand (1.2 mmol) [$C_{14}H_{17}N_3O_2$ (0.311 g), $C_{15}H_{19}N_3O_2$ (0.328 g), $C_{15}H_{19}N_3O_2$ (0.328 g)] dissolved in 25 mL of ethanol, the pH of the mixture changed as 3.0-3.5 and its color turned to red-brown. In order to raise the pH to 4.5, 1% NaOH solution in ethanol was added and the mixture was stirred in a water bath at $50-55^\circ C$ for 15 min. The precipitated complexes were filtered while they were hot, washed with water, ethanol and diethyl ether and dried at $100^\circ C$. The colors, yields and melting point of the compounds are given in table 1.

RESULTS AND DISCUSSION

In this study, starting with methylcyclohexylketone(1-acetyl-1-cyclohexene), anti-1-acetyl-1-cyclohexenylglyoxime was carried first by oxidation of the methyl group to the isonitroso group and, subsequently, conversion of $C=O$ to the oxime by condensation with hydroxylammonium chloride, as given in the literature¹⁸. Chlorination of this compound in chloroform afforded anti-1-acetyl-1-cyclohexenylchloroglyoxime ($C_8H_{11}ClN_2O_2$), an acceptable starting material to obtain various unsymmetrically substituted 1-acetyl-1-cyclohexenylglyoxime(Figure 1).

Fig. 1. Ligand Formula : $R^1 = C_6H_5-$, $R^2 = C_6H_5-CH_2-$, $R^3 = p-CH_3-C_6H_4-$

The reaction of $C_8H_{11}ClN_2O_2$ with three different arylamines in ethanol at $-15^\circ C$ gave three new substituted amino-1-acetyl-1-cyclohexenylglyoximes (Figure 2).

Fig.1a. Three dimensional structure of L1 ; R : C6H5-

Fig. 2. Square-planar metal complexes of anti- and cis- complexes; R1 = C6H5 -, R2 = C6H5-CH2- , R3 = p-CH3 - C6H4 -

Fig.2a. Three dimensional structure of $[Ni(HL1)_2]$, trans form; R = C6H5-

Table 1. ^1H n.m.r. spectra of the ligands and $[\text{Ni}(\text{L}^2)_2]$ in DMSO-d_6 δ (p.p.m.)

Compounds	O -H.....O ^a	O - H ^a	O - H ^a	H ^a	N - H ^a	Other
L^1H_2	-	11.95 (1H) s	10.62 (1H) s	8.15-6.85 (14H) m	8.65 (1H) s	-
L^2H_2	-	12.05 (1H) s	10.02 (1H) s	7.95-7.35 (14H) m	6.96 (1H) s	4.25-4.20 (-CH ₂) (2H) m
$[\text{Ni}(\text{L}^2)_2]$	14.15 (2H) s			7.55-7.05 (28H) m	8.05 (2H) m	4.30-4.25 (-CH ₂) (4H) m
L^3H_2	-	11.90 (1H) s	10.35 (1H) s	7.80-6.55 (13H) m	8.55 (1H) s	2.55 (-CH ₃) (3H) s

^aDisappears on D₂O exchange s: singlet m: multiplet**Table 2.** Colors, molecular weights, magnetic moments, m.p.s, yield and elemental analytical results for the ligands and their complexes

Compounds	Color and M.W	Yield (%)	M.p. (°C) (dec)	$\mu_{\text{eff}}(\text{BM})^{\text{I}}$	Calcd. (Found) %			
					C	H	N	M
L^1H_2	Yellow 259	80	105	-	64.86 (64.75)	6.56 (6.50)	16.22 (16.11)	-
$\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_2$								
$[\text{Ni}(\text{HL}^1)_2]$	Red 574,7	83	195	Dia	58.46 (58.50)	5.57 (5.45)	14.61 (14.40)	10.21 (10.18)
$\text{C}_{28}\text{H}_{32}\text{NiN}_6\text{O}_4$								
$[\text{Cu}(\text{HL}^1)_2]$	Dark Brown 579,5	72	173	1.20	57.98 (57.68)	5.52 (5.45)	14.50 (14.33)	10.96 (10.85)
$\text{C}_{28}\text{H}_{32}\text{CuN}_6\text{O}_4$								
L^2H_2	Cream 273	80	130	-	65.93 (65.81)	6.96 (6.82)	15.38 (15.25)	-
$\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_2$								
$[\text{Ni}(\text{HL}^2)_2]$	Red 602,7	85	190	Dia	59.78 (58.99)	5.97 (5.78)	13.94 (13.69)	9.74 (9.70)
$\text{C}_{30}\text{H}_{36}\text{NiN}_6\text{O}_4$								
$[\text{Cu}(\text{HL}^2)_2]$	Dark Brown 607,5	75	175	1.44	59.26 (59.15)	5.93 (5.86)	13.83 (13.70)	10.45 (10.37)
$\text{C}_{30}\text{H}_{36}\text{CuN}_6\text{O}_4$								
L^3H_2	Cream 273	85	123	-	65.93 (65.45)	6.96 (6.86)	15.38 (15.27)	-
$\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_2$								
$[\text{Ni}(\text{HL}^3)_2]$	Red 602,7	78	235	Dia	59.78 (59.60)	5.97 (5.63)	13.94 (13.63)	9.74 (9.62)
$\text{C}_{30}\text{H}_{36}\text{NiN}_6\text{O}_4$								
$[\text{Cu}(\text{HL}^3)_2]$	Dark Brown 607,5	70	185	1.40	59.26 (59.46)	5.93 (5.87)	13.83 (13.64)	10.45 (10.41)
$\text{C}_{30}\text{H}_{36}\text{CuN}_6\text{O}_4$								

^I μ_{eff} : Magnetic moment, Dia . Diamagnetic.**Table 3.** Characteristic i.r. bands of ligands and their complexes^a (KBr pellets)

Compounds	ν (N-H)	ν (O-H)	ν (C-H ^a)	ν (O-H....O)	ν (C=N)	ν (N-O)	ν (M-N)
L^1H_2	3370 b	3170 b	2860 m		1680 s	980 s	
$[\text{Ni}(\text{HL}^1)_2]$	3330 b		3070 m	1650 w	1600 s	940 s	490 w
$[\text{Cu}(\text{HL}^1)_2]$	3310 b		3070 m	1640 w	1610 s	930 s	480 w
L^2H_2	3420 b	3320 b	2890 m		1610 s	960 s	
$[\text{Ni}(\text{HL}^2)_2]$	3380 b		3050 m	1710 w	1630 s	950 s	495 w
$[\text{Cu}(\text{HL}^2)_2]$	3370 b		3070 m	1700 w	1620 s	940 s	500 w
L^3H_2	3370 b	3110 b	2900 m		1610 s	970 s	
$[\text{Ni}(\text{HL}^3)_2]$	3430 b		3050 m	1720 w	1600 s	950 s	490 w
$[\text{Cu}(\text{HL}^3)_2]$	3420 b		3050 m	1710 w	1620 s	940 s	500 w

Table 4. TGA data of the complexes

Compounds	First Step (°C) Weight Loss Calcd. (Found) %	Second Step(°C) Weight Loss Calcd. (Found) %	Third Step (°C) Weight Loss Calcd. (Found) %	Weight Loss Calcd. (Found) %	Residue (NiO, CuO) Calcd. (Found) %
[Ni(HL ¹) ₂]	432-545	545-590	590-723		
	31,67 (32,03)	36,71 (35,91)	18,61 (19,27)	87,00 (87,21)	13,00 (12,79)
[Cu(HL ¹) ₂]	362-462	462-533	533-719		
	31,40 (31,88)	36,41 (35,74)	18,48 (18,87)	86,29 (86,49)	13,71 (13,51)
[Ni(HL ²) ₂]	368-511	511-672	672-898		
	27,54 (26,95)	24,56 (25,02)	35,50 (34,53)	87,60 (86,50)	12,40 (13,50)
[Cu(HL ²) ₂]	391-496	496-573	573-801		
	27,33 (27,67)	24,36 (23,85)	35,22 (35,98)	86,91 (87,50)	13,09 (12,50)
[Ni(HL ³) ₂]	441-561	561-774	774-1086		
	27,54 (28,33)	24,56 (25,35)	35,50 (34,52)	87,60 (88,20)	12,40 (11,80)
[Cu(HL ³) ₂]	368-551	551-759	759-1066		
	27,33 (26,88)	24,36 (24,66)	35,22 (35,85)	86,91 (87,39)	13,09 (12,61)

¹H-n.m.r. spectra of the ligands

In the ¹H-n.m.r. spectra, two different –OH peaks were seen for these ligands (Table 1). These two deuterium exchangeable singlets correspond to two non equivalent structures which indicate the *anti*-configuration such as *cis* – and *trans* – form of this compound^{17, 19-20}. The chemical shift of the O-H protons is seen at 11.90-12.05 ppm and the N-H protons at 6.96-8.65 ppm. The losing of these peaks with the addition of D₂O to the solution guides that the observed chemical shifts belong to the protons of O-H and N-H groups. ¹H-n.m.r. for L²H₂ : 6.96ppm (N-H, 1H), 4.25 ppm, CH₂, 2H).

¹H-n.m.r. spectra of the complexes

The solubility of the complexes of the three new unsymmetrical ligands is not enough to obtain ¹H-n.m.r. spectra in solution except [Ni(HL²)₂]. The proton n.m.r. spectrum of this diamagnetic complex indicates the formation of O – H...H bridge by the strong shift of the peak of complex at 14.15 ppm and this obtained data were contrary to the L¹H₂^{10,20}. These values were given as 4.30 ppm (–CH₂, 4H), for Ni(II)complex. In conclusion of the unsymmetry in the ligands, the complexes are accepted to form two isomers (Fig 2). TLC (silicagel-G) was employed with different solvent mixtures and varying polarities, but only one spot appears in each case. This result implies that the formation of only one isomer is possible under these reaction conditions. The geometric isomerism of [Ni(HL¹)₂] can be inferred from the ¹H-n.m.r. spectrum, since the alternative chemical environments will show two O – H...O bridge protons in the *cis*-form, but only one of them is in the *trans*-structure. The observed spectrum has only one resonance at 14.15 ppm implying the *trans*-form of complex.

Magnetic properties

Magnetic susceptibility measurement provides information to characterize the structure as shown in Table 2. The mononuclear Ni(II) complexes of these ligands are diamagnetic as expected for a d⁸ metal ion in a square planer field^{20,21}. The Cu(II) complexes at 20 °C are paramagnetic, μ_{eff} = 1.20 – 1.44 BM.

Conductivity measurements

The molar conductance values of the synthesized ligands and their Ni(II) and Cu(II) complexes were measured and by the way it was seen that all the complexes are non-electrolytes.

I. r. spectra of ligands and complex

In the i.r. spectra of the ligands, –NH (3370-3420 cm⁻¹), OH (320-3110 cm⁻¹), C=N (1680-1610 cm⁻¹) and NO (980-960 cm⁻¹) stretches appear at frequencies expected for substituted glyoxime^{12,18,21} (Table 3). The characteristic i.r. absorptions of the complexes are given in Table 3. The range of the metal-ligand 1:2. From the results it can be said that Ni(II) and Cu(II) compounds were square-planar coordination as it is seen from Figure 2.. The i.r. spectra of

the complexes support these structures by weak bending vibration of the O – H ... O bridges around 1640-1720 cm⁻¹ and the shift of the C=N vibration to lower frequencies at 1600 -1630 cm⁻¹ due to N,N-metal coordination^{12,22}.

TGA Analysis of metal complexes

The TGA curves for the Ni(II) and Cu(II) complexes were obtained at a heating rate of 10 °C / min in a nitrogen atmosphere between the temperature range of 362-1086 °C. It was seen from the TGA results that decomposition of Ni(II) and Cu(II) complexes began between 362-441 °C and finished between 728-1086 °C. Ni(II) and Cu(II) complexes decompose to NiO and CuO in 3 steps in the temperature ranges. These results showed similarity with the results of other literatures²³⁻²⁶.

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