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Synthesis and Complex Formation of Some Novel *vic*-Dioxime Derivatives of Hydrazones

Nursabah SARIKAVAKLI[1]*, Gazi İREZ[2]
[1]*Department of Chemistry, Faculty of Arts and Sciences, Adnan Menderes University, 09010 Aydın-TURKEY*
e-mail: nsarikavakli@adu.edu.tr
[2]*Department of Chemistry, Faculty of Arts and Sciences, Uludağ University, 16059 Bursa-TURKEY*

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Three novel vic-dioxime compounds and their transition metal complexes were synthesized for the first time. These ligands are anti-glyoximehydrazine (GH_2), anti-2-pyridinealdehydeglyoxime hydrazone ($PyGH_2$) and anti-2-furancarboxaldehydeglyoxime hydrazone (FGH_2). The synthesized anti-glyoximehydrazine was reacted with 2-pyridinealdehyde or 2-furancarboxaldehyde to obtain the $PyGH_2$ and FGH_2ligands. Mononuclear complexes of these ligands with a metal-ligand ratio of 1:2 were prepared with Ni(II), Co(II) and Cu(II) ions. The structures of the ligands and complexes were determined by ^{1}H n.m.r, i.r spectroscopy and elemental analytical techniques.

Key Words: *vic*-Dioximes, Glyoximes, Hydrazone compounds, Metal complexes.

Introduction

The coordination chemistry of hydrazones is an intensive area of study and numerous transition metal complexes of these ligands have been investigated[1,2].

Hydrazone compounds obtained by the reaction of aromatic and heterocyclic hydrazides with mono- and di-aldehydes or ketones have revealed very versatile behavior in metal coordination[3]. Many researchers have synthesized a number of new hydrazones because of their ease of synthesis[4].

Hydrazones have been studied as a group of the most useful spectrophotometric reagents[4–6]. Combining appropriate starting materials (carbonyl compounds and hydrazine), the sensitivity as an analytical reagent and/or solubility of the hydrazones could be improved and the donating environment could be changed. The shortcoming of hydrazones was their lack of selectivity[4]for metal ions. Much effort has been devoted to developing masking agents for use with hydrazones[7,8].

High-performance liquid chromatography (HPLC) of metal chelates[9] is a promising alternative approach for overcoming the lack of selectivity of the chelating reagents[4]. Hydrazone ligands and their com-

*Corresponding author

plexes have been studied for their antifungal and antibacterial activity, as iron chelators in the treatment of anemias and as antiviral drugs[3].

vic-Dioximes have not only produced stable metal complexes of transition, inner-transition and actinide metal ions, these ligands and their metal complexes have also played a significant role in the domains of stereochemistry, structure, isomerism, magnetism, spectroscopy, model systems of biochemical interest, cation exchange and ligand exchange chromatography, analytical chemistry, catalysis, stabilizers, polymers and pigments and dyes[1,2].

Many studies have been camed out into hydrazones, and mono- and di-oximes. Little information related to the derivatives of *vic*-dioxime with hydrazone side groups was found, in the literature.

The novel *anti*-glyoximehydrazine (GH_2), *anti*-2-pyridinealdehydeglyoxime hydrazone ($PyGH_2$) and *anti*-2-furancarboxaldehydeglyoxime hydrazone (FGH_2), and their complexes with Ni(II), Co(II) and Cu(II) ions are described.

Experimental

Materials and Instrumentation

All reagents used were purchased from Merck and used as received. Elemental analyses, ^{1}H n.m.r spectra (Bruker 400 MHz), i.r spectra (Pye-Unicam SP-1025), melting points (Buchi SPM-20) and pH measurements (Orion Expandable Ion Analyzer EA 940) were used to elucidate the structures of the products. The magnetic moments of the complexes were measured by the Gouy method with a Newport type D-104 instrument magnet power supply (293 K).

Preparation of the Compounds

anti-Chloroglyoxime was prepared according to previously published procedures[10]

Synthesis of *anti*-Glyoximehydrazine (GH_2)

A solution of (0.4 g, 10 mmol) NaOH in 1 mL of water was mixed with 10 mL of ethanol and 0.6 mL of hydrazinium hydroxide (80%, d = 1.03 g/mL) and cooled to 0 °C. A solution of *anti*-chloroglyoxime (1.225 g, 10 mmol) dissolved in 5 mL of ethanol was added dropwise into the prepared mixture with stirring at the same temperature. At the end of the addition the ligand started to precipitate. Stirring was continued for 15 min at the same temperature to complete the reaction. The precipitate was filtered, washed with cold ethanol and dried in a vacuum oven. Yield was 1.06 g (90%). The compound decomposes easily. After 24 h it may decompose even at room temperature in a vacuum oven. This ligand is soluble in water, DMF, DMSO and pyridine.

Synthesis of *anti*-2-Pyridinealdehydeglyoxime Hydrazone ($PyGH_2$)

A cooled (5 °C) solution of (0.54 mL, 5 mmol) 2-pyridinealdehyde in 10 mL of ethanol was added dropwise into a cooled solution (5 °C) containing GH_2(0.59 g, 5 mmol) and 3-5 drops of CH_3COOH in 10 mL of water with constant stirring. After the addition of 2-pyridinealdehyde was completed, the mixture was stirred for

Table 1. Magnetic moments, characteristic i.r bands[a] of the ligands and their Ni(II), Cu(II) and Co(II) complexes as KBr pellets cm^{-1}.

Compounds	Mag. Mom. (per metal)[a] B.M	$\nu(NH_2)$	ν(N-H)	ν(O-H)	ν(C=N) Oxime	ν(C=N) Hydrazone	ν(N-O)	ν(C-H) Aliph.	ν(C-H) Arom.	ν(C-H) Aldehyde	ν(OH-O)
GH_2	-	3340 (m)	3320 (b)	3290 (b)	1625 (s)	-	1000 (s)	2910 (w)	-	-	-
$(GH)_2Ni$	Diamagnetic	3330 (m)	3300 (b)	-	1620 (s)	-	990 (s)	2920 (w)	-	-	2200 (w)
$(GH)_2Co$	2.11	3340 (m)	3310 (b)	-	1615 (s)	-	980 (s)	2910 (w)	-	-	2300 (w)
$(GH)_2Cu$	1.15	3340 (m)	3300 (b)	-	1620 (s)	-	990 (s)	2910 (w)	-	-	2320 (w)
$PyGH_2$	-	-	3450 (b)	3260 (b)	1625 (s)	1670 (m)	1010 (s)	2910 (w)	3060 (w)	2930 (w)	-
$(PyGH)_2Ni$	Diamagnetic	-	3400 (b)	-	1610 (s)	1640 (m)	1000 (s)	2920 (w)	3010 (w)	2920 (w)	2200 (w)
$(PyGH)_2Co$	2.68	-	3410 (b)	-	1610 (s)	1645 (m)	990 (s)	2910 (w)	3010 (w)	2900 (w)	2320 (w)
$(PyGH)_2Cu$	1.69	-	3410 (b)	-	1615 (s)	1645 (m)	990 (s)	2910 (w)	3000 (w)	2910 (w)	2330 (w)
FGH_2	-	-	3430 (b)	3290 (b)	1625 (s)	1650 (m)	970 (s)	2940 (w)	3040 (w)	2920 (w)	-
$(FGH)_2Ni$	Diamagnetic	-	3400 (b)	-	1615 (s)	1645 (m)	970 (s)	2830 (w)	3030 (w)	2910 (w)	2320 (w)
$(FGH)_2Co$	2.90	-	3410 (b)	-	1640 (s)	1640 (m)	970 (s)	2840 (w)	3040 (w)	2890 (w)	2300 (w)
$(FGH)_2Cu$	1.59	-	3420 (b)	-	1620 (s)	1640 (m)	965 (s)	2840 (w)	3040 (w)	2910 (w)	2200 (w)

[a] by using molar susceptibility.

b = broad, s = strong, m = medium, w = weak.

Table 2. Analytical and physical data for ligands and their complexes.

Compounds	Formulaes (MW)	Colors	M.p[a].(^{o}C)	Yield (%)	Calculated (Found) %			
					C	**H**	**N**	**M**
GH_2	$C_2H_6N_4O_2$	Yellow	71	90	20.34	5.12	47.44	-
	(118.10 g)				-20.59	-4.96	-47.74	
$(GH)_2Ni$	$C_4H_{10}N_8O_4Ni$	Red	240	50	16.4	3.44	38.26	20.04
	(292.86 g)				-16.02	-3.23	-38.19	-20.36
$(GH)_2Co$	$C_4H_{10}N_8O_4Co$	Red-Brown	210	55	16.39	3.44	38.23	20.1
	(293.11 g)				-16.27	-3.25	-38	-20.08
$(GH)_2Cu$	$C_4H_{10}N_8O_4Cu$	Dark-Brown	238	52	16.14	3.39	37.64	21.3
	(297.01 g)				-16.06	-3.24	-37.61	-21.53
$PyGH_2$	$C_8H_9N_5O_2.2H_2O$	Cream	110	82	39.49	5.39	28.8	-
	(243.10 g)				-39.44	-5.51	-28.67	
$(PyGH)_2Ni$	$C_{16}H_{16}N_{10}O_4Ni$	Red-Brown	205	67	40.84	3.43	29.79	12.32
	(470.10 g)				-40.53	-3.25	-29.63	-12.61
$(PyGH)_2Co$	$C_{16}H_{16}N_{10}O_4Co$	Dark-Brown	213	54	40.76	3.42	29.73	12.5
	(471.07 g)				-40.48	-3.65	-29.6	-12.14
$(PyGH)_2Cu$	$C_{16}H_{16}N_{10}O_4Cu$	Dark-Brown	215	70	40.38	3.37	29.44	13.35
	(475.05 g)				-40.08	-3.09	-29.19	-13.16
FGH_2	$C_7H_8N_4O_3$	Dark-Yellow	150	60	42.84	4.11	28.57	-
	(196.06 g)				-42.69	-4.32	-28.48	
$(FGH)_2Ni$	$C_{14}H_{14}N_8O_6Ni$	Dark-Red	284	83	37.5	3.15	25	12.93
	(448.04 g)				-37.25	-3.03	-24.68	-12.98
$(FGH)_2Co$	$C_{14}H_{14}N_8O_6Co$	Dark-Brown	245	66	37.41	3.14	24.95	13.1
	(449.04 g)				-37.66	-3.45	-24.68	-13.08
$(FGH)_2Cu$	$C_{14}H_{14}N_8O_6Cu$	Brown	262	75	37.08	3.11	24.73	13.8
	(453.03 g)				-36.88	-3.38	-24.48	-14.15

[a]with decomposition

Table 3. ^{1}H-n.m.r spectra of the ligands[a,b] and $(GH)_2Ni$, $(PyGH)_2Ni$ and $(FGH)_2Ni$ in DMSO-d_6 in δ (ppm).

Compounds	H-O...H	O-H[c]	N-H[c]	N=CHR	-NH_2	C*H*=NOH	CH (Furan)	CH (Pyridine)
GH_2	-	10.4 and 10.2 (1H each, 2s)	11.1 (1H, t)	-	4.8 (2H, d)	8.5 (1H, s)	-	-
$PyGH_2$	-	10.6 and 10.4 (1H each, 2s)	11.5 (1H, s)	8.2 (1H, s)	-	8.6 (1H, s)	-	8.5 (1H,dd)[d] 8.0 (2H, m) 7.4 (1H,dd)[d]
FGH_2	-	10.3 and 10.0 (1H each, 2s)	11.2 (1H, s)	7.9 (1H, s)	-	8.5 (1H, s)	7.3 (1H, dd)[e] 6.4 (1H, dd)[e] 7.6 (1 dd)[e]	-
$(GH)_2Ni$	15.31	-	10.9 (1H,t)	-	4.85 (2H,d)	8.47 (1H,s)	-	-
$(PyGH)_2Ni$	15.4	-	11.4 (1H,s)	8.21 (1H,s)	-	8.56 (1H,s)	-	8.48 (1H,dd)[d] 7.98 (2H, m) 7.37 (1H,dd)[d]
$(FGH)_2Ni$	15.42	-	11.15 (1H,s)	8.22 (1H, s)	-	8.45 (1H, s)	7.27 (1H, dd)[e] 6.35 (1H, dd)[e] 7.55 (1 dd)[e]	-

[a]Chemical shifts (δ) are reported in ppm relative to $SiMe_4$ at 30 °C, s: singlet. d: doublet, t: triplet, m: multiplet, [b]in DMSO-d_6, [c]Disappears on D_2O exchange. 1: [a]J = 8 Hz, 2: [e]J = 3.5 Hz.

an additional 30 min at room temperature. Then the cream colored precipitate was filtered, washed with water and dried at room temperature in a vacuum oven. Yield was 1.69 g (82%). This ligand is soluble in ethanol, pyridine and DMF and slightly soluble in DMSO.

Synthesis of *anti*-2-Furancarboxaldehydeglyoxime Hydrazone (FGH_2)

A solution of freshly distilled 2-furancarboxyaldehyde (0.42 mL, 5 mmol) in ethanol (10 mL) was added dropwise into a solution of GH_2 (0.59 g, 5 mmol) dissolved in 10 mL of water containing 3-5 drops CH_3COOH at 5 °C. After the addition of 2-furancarboxyaldehyde was completed, the solution was stirred for an additional 30 min.

Then the yellow precipitate was filtered, washed with water and dried at room temperature in a vacuum oven. Yield was 1 g (60%). This ligand is soluble in ethanol and slightly soluble in pyridine, DMF and DMSO.

Preparation of the Transition Metal Complexes of GH_2, $PyGH_2$ and FGH_2

A solution of a metal salt (1 mmol of $NiCl_2.6H_2O$, $CoCl_2.6H_2O$ or $CuCl_2.2H_2O$) in 20 mL of water was added to 2 mmol of the GH_2 ligand solution (0.236 g, in 15 mL of water or $PyGH_2$, 0.486 g, and FGH_2, 0.392 g, in 15 mL of ethanol) with stirring. An initial sharp decrease in the pH of the solution from 5.5 to about 3-3.5 was observed. After raising the pH to 5-5.5 using a 1% aqueous NaOH solution, the reaction mixture was kept in a hot water bath (80 °C) for 15 min to complete the precipitation. Then the precipitated complex compounds were filtered, washed with hot water and dried at room temperature in a vacuum oven. The complexes are slightly soluble in DMF and DMSO.

Results and Discussion

Three novel *vic*-dioxime compounds, *anti*-glyoximehydrazine (GH_2), *anti*-2-pyridinealdehydeglyoxime hydrazone ($PyGH_2$) and *anti*-2-furancarboxaldehyde glyoxime hydrazone (FGH_2) were synthesized. *anti*-Glyoximehydrazine (GH_2) was synthesized by the reaction of *anti*-chloroglyoxime and hydrazinium hydroxide in an alcohol-water mixture (4:1). The synthesized *anti*-glyoximehydrazine was reacted with 2-pyridinealdehyde or 2-furancarboxaldehyde to obtain the $PyGH_2$ and FGH_2ligands, respectively (Scheme). In addition the complexes of these ligands with Ni(II), Co(II) and Cu(II) ions were prepared (Figures a,b).

The characteristic i.r. bands of the ligands are given in Table l. The characteristic O-H, C=N, N-H and N-O stretching vibration bands of the ligands are observed at 3290 (b), 1625 (s), 3320 (b) and 1000 (s) cm^{-1} for GH_2, 3260 (b), 1625 (s), 3450 (b) and 1010 (s) cm^{-1} for $PyGH_2$ and 3290 (b), 1625 (s), 3430 (b) and 970 (s) cm^{-1} for FGH_2, respectively. These values are in accordance with those of similar compounds previously reported in the literature[2,11,12].

Elemental analyses, i.r. and magnetic susceptibility were used to illuminate the structures of the complexes. Some physical properties and elemental analytical data of the ligands and complexes are given in Table 2.

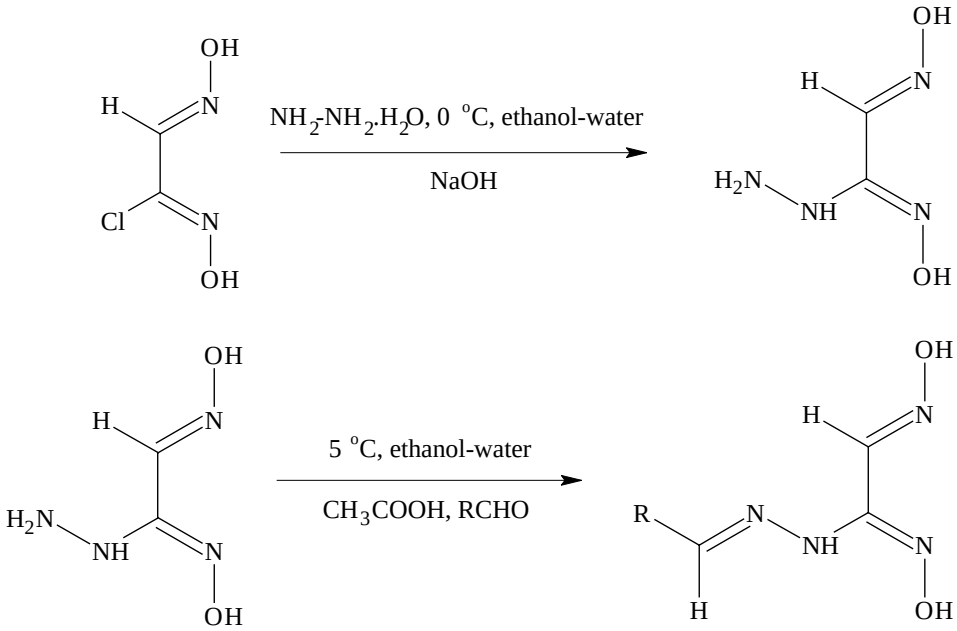
The mononuclear complexes of Ni(II), Co(II) and Cu(II) ions with the ligands GH_2, $PyGH_2$ and FGH_2 are suggested to be square-planar with a metal-ligand ratio of 1:2. It is known that Ni(II), Co(II) and Cu(II) metal complexes of dimethylglyoxime are 5- membered chelate structures and the metal ion

coordinates to the nitrogen atoms of the dioxime groups. A hydrogen atom separates each of the 2 oxime groups, and as a result a hydrogen bridge is established. The hydrogen bridge (O-H...O) bonds[13,14] of the $(GH)_2M$, $(PyGH)_2M$ and $(FGH)_2M$ complexes appear at 2320-2200, 2330-2200 and 2320-2200 cm^{-1}, respectively. Deformation bands of the hydrogen bonds are observation at 1700 cm^{-1}. These values are in good agreement with those reported in the literature for square-planar complexes of Ni(II), Co(II) and Cu(II) ions[15−20]. Furthermore, the observance of C=N bands of the ligands at 1625 cm^{-1} and those of the complexes at a lower field indicates that the nitrogen atoms of the C=N groups participate in the complex formation.

The magnetic susceptibility measurements of $(GH)_2M$, $(PyGH)_2M$ and $(FGH)_2M$ indicate that the Ni(II) complexes are diamagnetic and the magnetic moments of the Cu(II) and Co(II) complexes are 1.69-1.15 and 2.11-2.90 B.M., respectively. These results are in good agreement with the square-planar structures of the complexes[21].

The ^{1}H-n.m.r. spectral data of the ligands and complexes are given in Table 3. When the ^{1}H-n.m.r spectra of the ligands in DMSO-d_6 are examined, 2 singlets corresponding to the 2 N-OH protons of the ligand (at 10.4 ppm and 10.2 ppm for GH_2 10.3 ppm and 10.0 ppm for FGH_2 and 10.6 ppm and 10.4 ppm for $PyGH_2$) are observed.

Observation of 2 different ^{1}H-n.m.r signals for N-OH protons and the red color of the Ni(II) complexes indicate that the *vic*-dioxime is in the *anti*-form[2,11,12]. The disappearance of these signals by addition of D_2O to the ligand solution indicates that the observed resonances are those of the protons of O-H and N-H groups. These values are in good agreement with those reported in the literature[15,16,22−25]. C-H protons neighboring on oxime groups are observed at 8.5-8.6 ppm[13,15,22,26]. In addition the aldehyde RC*H*=NOH proton appears as a singlet in the same area.



R = 2-Furyl, (FGH_2) or 2-Pyridyl, ($PyGH_2$)

Scheme

Because of the asymmetry in the ligands, the complexes are expected to form 2 isomers: *trans-* and *cis-* (Figures a and b). The ^{1}H-n.m.r spectrum of the Ni(II) complexes may be evaluated to determine the isomer formed, since the various chemical environments will show 2 O-H. . . O bridge protons for the *cis*-form, but only 1 for the *trans*-structure. The observed ^{1}H-n.m.r spectrum of the 2 nickel complexes has only 1 signal at 15.31, 15.40 and 15.42 ppm, which confirms the *trans*-form of the complexes[22,27].

On the basis of the above data, it is concluded that the prepared complexes are dsp^2 hybridized and square-planar, as shown in Figures a and b.

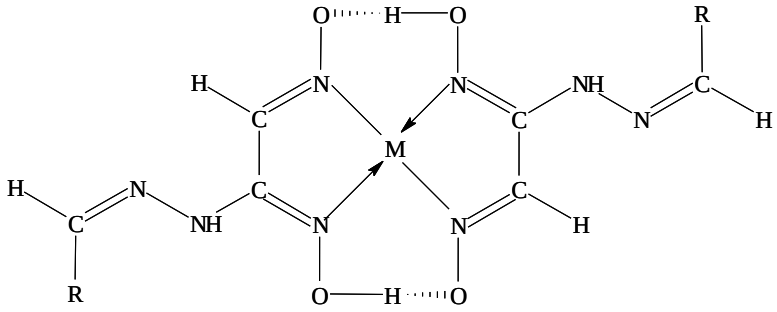


Figure a: trans-form.

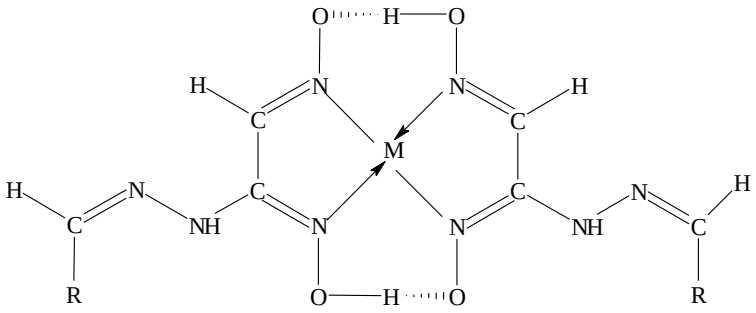


Figure b: cis-form.

Trans-(1*Z*)-acetaldehyde {10-[(2*Z*)-2-ethylidenehydrazino]-1,6,8,13-tetraoxa-2,5,9,12-tetraazacyclotetradeca-2,4,9,11-tetraen-3-yl}hydrazone compound with metal (1:1)

Cis- (1*Z*)-acetaldehyde {11-[(2*Z*)-2-ethylidenehydrazino]-1,6,8,13-tetraoxa-2,5,9,12-tetraazacyclotetradeca-2,4,9,11-tetraen-3-yl}hydrazone compound with metal (1:1)

M = Ni(II), Cu(II) and Co(II)

R = 2-Furyl, $(FGH)_2M$ or 2-Pyridyl, $(PyGH)_2M$

Figure. Suggested structure of the complexes of Ni(II), Cu(II), Co(II).

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