

Synthesis, Characterization of Some Co(III) Complexes with *vic*-Dioxime Ligands and Their Antimicrobial Properties

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In this study, 6 different new *vic*-dioxime ligands and their mononuclear complexes with Co(III) have been synthesized. The structures of these compounds were identified by using elemental analyses, IR, ¹H and ¹³C NMR, electronic spectra, magnetic susceptibility measurements and conductivity. In addition, the thermal characterizations and antimicrobial activities of the ligands and their complexes have been investigated.

Key Words: *vic*-Dioxime ligands, cobalt(III) complexes, antimicrobial activities

Introduction

The chemistry of transition -metal complexes with *vic*-dioxime ligands has been well studied and is the subject of several reviews^{1,2}. The coordination compounds of *vicinal* dioximes have been widely investigated as analytical reagents³, models for biological systems⁴ such as vitamin B₁₂, compounds with columnar stacking thought to be behind their semiconducting properties⁵ and recently in *vic*-dioxime reactions⁶. Among the 3 isomers, namely *anti*-, *amphi*- and *syn*-, the first is more liable to form N,N-coordinated planar complexes stabilized by hydrogen bonding⁷. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms make *vic*-dioximes amphoteric ligands that form corrin-type, square-planar, square pyramidal and octahedral complexes with transition metal ions such as Ni(II), Cu(II), Co(II) and Co(III) as central atoms⁸. Metal ions play an important role in bioinorganic chemistry and metals such as Fe, Co, Ni, Cu, Zn and Cd may exist in trace amounts in biological systems. Structural studies of the complexes of these metals with biological compounds are extremely important. In order to understand the role of these metal ions it is useful to study analogous complexes such as metal dimethylglyoxime chalets^{9,10}.

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In our previous studies we investigated the synthesis and characterization of various transition metal complexes of new *vic*-dioximes¹¹⁻²¹. In this paper, we describe the synthesis and characterization of new *vic*-dioxime ligands and their mononuclear Co(III) complexes.

Experimental

The preparation of *anti*-chloroglyoxime has been described previously²². All the reagents used were purchased from the Merck, Fluka or Sigma companies and were chemically pure. Elemental analyses (C, H and N) were performed on a LECO-932 CHNSO elemental analyses apparatus. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer as KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz high performance digital FT-NMR spectrometer. Electronic spectra were obtained on a Shimadzu 1240 UV spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature using Hg[Co(SCN)₄] as a calibrate; diamagnetic corrections were calculated from Pascal's constants. The melting points were determined on a Gallenkamp melting point apparatus. Molar conductance of the *vic*-dioxime ligands and their transition metal complexes were determined at room temperature using a CMD 750 WPA conductivity meter. The metal contents of the complexes were determined with an ATI Unicam (Model 929) atomic absorption spectrophotometer in solutions prepared by decomposition of the compounds in conc. HCl and conc. HNO₃ (3:1) solution followed by dilution in water. TGA curves were recorded on a Shimadzu TG-50 thermobalance.

Preparation of the ligands

The synthesis and characterization of the ligands used in this study have been described previously¹¹⁻¹⁴. A solution of NaHCO₃ (3.40 g, 40 mmol) in absolute ethanol (50 mL) was added to a solution of [*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]ethane-1,2-diamine (5.23 g, 30 mmol) or *N*-[(2-ethyl-2-methyl-1,3-dioxolan-4-yl)methyl]ethane-1,2-diamine (5.65 g, 30 mmol) or *N*-(1,4-dioxaspiro[4.4]non-2-ylmethyl)ethane-1,2-diamine (6.00 g, 30 mmol) or *N*-(1,4-dioxaspiro[4.5]dec-2-ylmethyl)ethane-1,2-diamine (6.43 g, 30 mmol) or *N*-[(2-phenyl-1,3-dioxolan-4-yl)methyl]ethane-1,2-diamine (6.67 g, 30 mmol) or *N*-[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]ethane-1,2-diamine (7.09 g, 30 mmol)] in absolute ethanol (50 mL). Then a solution of *anti*-chloroglyoxime^{12-14,19} (3.70 g, 30 mmol) in absolute ethanol (45 mL) was added dropwise to the mixture at room temperature over 3 h. The mixture was stirred in a water bath at 50-60 °C for 4 h, filtered and then the ethanol was removed by evaporation. The oily product was dissolved in absolute methanol and precipitated by diethyl ether. The obtained product was filtered, washed with diethyl ether several times and dried in vacuum for 10 h. The compounds were found to be soluble in CH₂Cl₂, DMSO, DMF and methanol and insoluble in diethyl ether, *n*-hexane and benzene

Preparation of Co(III) complexes of the ligands

A quantity of 1.00 mmol ligands [H₂L¹ (0.63 g), H₂L² (0.66 g), H₂L³ (0.68 g), H₂L⁴ (0.71 g), H₂L⁵ (0.73 g), H₂L⁶ (0.76 g),] were dissolved in absolute ethanol (15 mL). A solution of 0.50 mmol metal salt CoCl₂·6H₂O (0.12 g) in absolute ethanol (15 mL) was added dropwise to the ligands solution with continuous stirring at 50 °C. The pH dropped to around 3.00-4.00 and then rose to 5.00-5.50 by the addition of a 1M NaOH

solution in ethanol. The reaction mixture was kept stirring at this temperature for 3 h, filtered and the precipitate washed in water, ethanol and diethyl ether and dried in vacuum at 60 °C. All the complexes are soluble in water, CHCl₃, EtOH, DMF and DMSO and insoluble in toluene, diethyl ether and *n*-hexane.

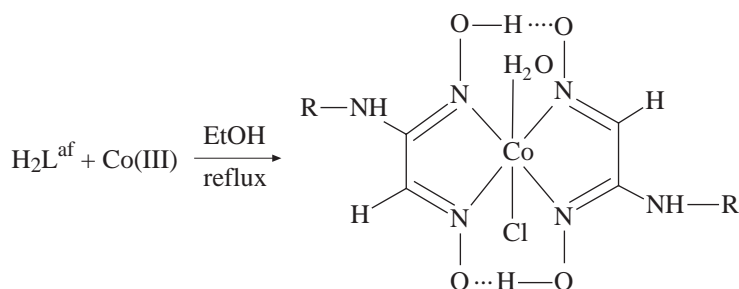
Preparation of microbial cultures

The antimicrobial activities of the compounds were determined in vitro using different microorganisms by the standard agar diffusion method²³. The following bacteria and yeast were used: *Enterobacter aeruginosa* CCM 2531, *Pseudomonas aeruginosa* DSM 50071, *Escherichia coli* ATCC 25922, *Staphylococcus aureus* COWAN I, *Saccharomyces cerevisiae* FMC 16, *Candida albicans* FMC 17 and *Bacillus subtilis niger*. Bacterial and fungal species were obtained from the Department of Microbiology's Laboratory of Biology of the Faculty of Arts and Sciences at Firat University. Bacteria was incubated at 37 °C for 24 h in nutrient broth medium (Difco), and the yeast were incubated in malt extract broth (Difco) for 48 h. The dilution plate method was used to enumerate microorganisms (10⁵ bacteria per mL) and yeasts (10³-10⁴ yeasts per mL)²⁴. Each culture (0.1 mL) was then inoculated aseptically and was well mixed by gentle shaking before pouring into the sterilized petri dishes. Wells of 9 mm size were then cut in the medium. To each of these, a solution of 100 µg of compound was added. All the compounds were dissolved in DMSO and were examined at a concentration of 0.05 g/mL. At the end of the incubation period the inhibition zones were measured in mm. DMSO was used as a control. *Azithromycin* (15 µg) AZM 15 was used reference standard²⁵. The zones of growth inhibition around the cup were measured after 18 h of incubation at 37 °C.

Results and Discussion

In this study, 6 *vic*-dioxime ligands used *N*-(2-[[2,2-dimethyl-1,3-dioxolan-4-yl)methyl]amino}ethyl)-*N'*-hydroxy-2-(hydroxyimino)ethanimidamide (**H₂L^a**), *N*-(2-[[2-ethyl-2-methyl-1,3-dioxolan-4-yl)methyl]amino}ethyl)-*N'*-hydroxy-2-(hydroxyimino)ethanimidamide (**H₂L^b**), *N*-{2-[(1,4-dioxaspiro[4.4]non-2-ylmethyl)amino]ethyl}-*N'*-hydroxy-2-(hydroxyimino)ethanimidamide (**H₂L^c**), *N*-{2-[(1,4-dioxaspiro[4.5]dec-2-ylmethyl)amino]ethyl}-*N'*-hydroxy-2-(hydroxyimino)ethanimidamide (**H₂L^d**), *N'*-hydroxy-2-(hydroxyimino)-*N*-(2-[[2-phenyl-1,3-dioxolan-4-yl)methyl]amino}ethyl)ethanimidamide (**H₂L^e**) and *N'*-hydroxy-2-(hydroxyimino)-*N*-(2-[[2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]amino}ethyl)ethanimidamide (**H₂L^f**) were obtained in good yield by literature methods¹¹⁻¹⁴. The compounds were characterized on the basis of IR, ¹H and ¹³C NMR spectra, magnetic susceptibility measurements, conductivity measurements and elemental analysis data. The thermal properties of the Co(III) complexes were studied by thermogravimetric analyses.

The mononuclear Co(III) complexes of the *vic*-dioxime were prepared to a 57-63% yield by treating CoCl₂·6H₂O in an absolute EtOH mixture with the ligands in the presence of a base such as NaOH. Co(III) complexes have a metal:ligand ratio of 1:2 according to the elemental analysis results. In the IR spectrum of mononuclear Co(III) complexes, the weak deformation band associated with intra-molecular hydrogen bonding was observed around 1700-1725 cm⁻¹²⁶. The other characteristic stretching vibrations belonging to N-H, C=N and N-O groups were observed around 3310-3385, 1610-1645 and 970-990 cm⁻¹, respectively²⁷. In all the Co(III) complexes a chloride ion and a water molecule are also coordinated to metal ions. The coordinated H₂O molecule is identified by a broad O-H absorption around 3450-3500 cm⁻¹ that keeps its intensities even after heating at 110 °C for 24 h.



$\text{H}_2\text{L}^{\text{a-f}}$	$\text{H}_2\text{L}^{\text{a}}$	$\text{H}_2\text{L}^{\text{b}}$	$\text{H}_2\text{L}^{\text{c}}$	$\text{H}_2\text{L}^{\text{d}}$	$\text{H}_2\text{L}^{\text{e}}$	$\text{H}_2\text{L}^{\text{f}}$
R	$\text{C}_8\text{H}_{17}\text{NO}_2$	$\text{C}_9\text{H}_{19}\text{NO}_2$	$\text{C}_{10}\text{H}_{19}\text{NO}_2$	$\text{C}_{11}\text{H}_{21}\text{NO}_2$	$\text{C}_{12}\text{H}_{17}\text{NO}_2$	$\text{C}_{13}\text{H}_9\text{NO}_2$

Scheme

The ^1H NMR spectra of the DMSO- d_6 solution of the ligands provided well-resolved signals, as expected. The oxime proton and NH signals around 7.62-11.10 and 5.61-6.50 ppm indicate that the oxime groups are in the (E,E) form^{12,26}. In the ^{13}C NMR spectra, the C=NOH groups in the ligands show 2 peaks around 146.00-152.39 ppm. These values are in good agreement with those of *vic*-dioximes^{13,27}.

Table 1. Analytical and physical data of the Co(III) complexes.

Compounds	Formula (F.W.) g/mol	Color	M.P. ($^{\circ}\text{C}$)	Yield (%)	Calculated (Found) %			
					C	H	N	M
$[\text{Co}(\text{HL}^{\text{a}})_2(\text{H}_2\text{O})(\text{Cl})]$	$\text{C}_{20}\text{H}_{40}\text{ClCoN}_8\text{O}_9$ 631.06	brown	227	59 (37.70)	38.06 (6.79)	6.40 (18.09)	17.76 (8.99)	9.34
$[\text{Co}(\text{HL}^{\text{b}})_2(\text{H}_2\text{O})(\text{Cl})]$	$\text{C}_{22}\text{H}_{44}\text{ClCoN}_8\text{O}_9$ 659.12	brown	193	57 (39.72)	40.09 (7.11)	6.74 (16.68)	17.00 (9.35)	8.94
$[\text{Co}(\text{HL}^{\text{c}})_2(\text{H}_2\text{O})(\text{Cl})]$	$\text{C}_{24}\text{H}_{44}\text{ClCoN}_8\text{O}_9$ 683.14	dark brown	201 (41.81)	60 (6.88)	42.19 (16.76)	6.51 (8.94)	16.41	8.63
$[\text{Co}(\text{HL}^{\text{d}})_2(\text{H}_2\text{O})(\text{Cl})]$	$\text{C}_{26}\text{H}_{48}\text{ClCoN}_8\text{O}_9$ 707.16	dark brown	176 (44.51)	58 (5.95)	44.16 (16.11)	6.28 (7.97)	15.85	8.33
$[\text{Co}(\text{HL}^{\text{e}})_2(\text{H}_2\text{O})(\text{Cl})]$	$\text{C}_{28}\text{H}_{40}\text{ClCoN}_8\text{O}_9$ 727.14	dark brown	198 (45.97)	61 (5.92)	46.25 (15.77)	5.56 (7.83)	15.41	8.10
$[\text{Co}(\text{HL}^{\text{f}})_2(\text{H}_2\text{O})(\text{Cl})]$	$\text{C}_{30}\text{H}_{44}\text{ClCoN}_8\text{O}_9$ 755.20 755.20	light brown	189 (48.02)	63 (6.24)	47.71 (15.22)	5.89 (8.18)	14.84	7.80

Table 2. Characteristic IR bands (cm^{-1})^a of the Co(III) complexes

Compounds	$\nu(\text{H}_2\text{O})$	$\nu(\text{N-H})$	$\nu(\text{C-H})$	$\nu(\text{O}\cdots\text{HO})$	$\nu(\text{C=N})$	$\nu(\text{N-O})$
$[\text{Co}(\text{HL}^{\text{a}})_2(\text{H}_2\text{O})(\text{Cl})]$	3500 s	3310 m	2876-2978 m	1715 w	1625 s	970 w
$[\text{Co}(\text{HL}^{\text{b}})_2(\text{H}_2\text{O})(\text{Cl})]$	3485 s	3350 m	2870-2965 m	1700 w	1630 s	972 w
$[\text{Co}(\text{HL}^{\text{c}})_2(\text{H}_2\text{O})(\text{Cl})]$	3492 s	3320 m	2871-2960 m	1720 w	1640 s	980 w
$[\text{Co}(\text{HL}^{\text{d}})_2(\text{H}_2\text{O})(\text{Cl})]$	3480 s	3335 m	2866-2970 m	1725 w	1645 s	990 w
$[\text{Co}(\text{HL}^{\text{e}})_2(\text{H}_2\text{O})(\text{Cl})]$	3450 s	3385 m	2875-3075 m	1705 w	1620 s	977 w
$[\text{Co}(\text{HL}^{\text{f}})_2(\text{H}_2\text{O})(\text{Cl})]$	3490 s	3340 m	2870-3080 m	1710 w	1610 s	983 w

^a s: strong, m: medium, w: weak

The electronic spectrum of the Co(III) complexes shows 2 bands around 411-604 nm, which may be assigned to $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$ and $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$ transition. There are absorptions around 340-355 nm, which are ascribed to metal-to-ligand charge transfer²⁸. The u.v.-visible peaks corresponding to the $\pi \rightarrow \pi^*$

and $n \rightarrow \pi^*$ transitions in these ligands, and these were observed around 270-305 nm. The peaks belonging to the $\pi \rightarrow \pi^*$ transitions are shifted to a longer wavelength as a consequence of coordination and this confirms the formation of Co(III) complexes²⁹. Magnetic measurements were recorded at room temperature. Magnetic susceptibility measurements provide sufficient information to characterize the structures as shown in (Table 3). The Co(III) complexes are paramagnetic, and their magnetic susceptibility values are around 4.20-4.71 B.M. The values indicated are in good agreement with the literature³⁰. These results indicate an octahedral geometry for the Co(III) complexes. The suggested structures of the complexes are shown in the Scheme.

Table 3. Magnetic moment, molar conductance and electronic spectral data of the ligands and Co(III) complexes.

Compounds	μ_{eff}/atom (B.M.)	Λ_M ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) ^a	λ_{max} (nm) ^a
H ₂ L ^a	—	2.1	290
H ₂ L ^b	—	1.9	295
H ₂ L ^c	—	1.6	288
H ₂ L ^d	—	3.0	294
H ₂ L ^e	—	2.8	305, 282
H ₂ L ^f	—	3.4	300, 270
[Co(HL ^a) ₂ (H ₂ O)(Cl)]	4.33	8.2	580, 425, 349
[Co(HL ^b) ₂ (H ₂ O)(Cl)]	4.71	8.9	568, 411, 345
[Co(HL ^c) ₂ (H ₂ O)(Cl)]	4.50	7.7	570, 415, 340
[Co(HL ^d) ₂ (H ₂ O)(Cl)]	4.44	6.9	604, 422, 350
[Co(HL ^e) ₂ (H ₂ O)(Cl)]	4.20	9.4	570, 419, 355 283
[Co(HL ^f) ₂ (H ₂ O)(Cl)]	4.62	10.3	565, 420, 351 277

^ain DMSO

Table 4. TGA data of the Co(III) complexes.

Compounds	First Step (°C)	Second Step (°C)	Third Step (°C)	Residue (CoO) Calculated (Found) %
	Weight Loss Calculated (Found) %	Weight Loss Calculated (Found) %	Weight Loss Calculated (Found) %	
[Co(HL ^a) ₂ (H ₂ O)(Cl)]	38-150 2.85 (3.37)	150-301 36.44 (37.01)	301-623 48.84 (47.02)	88.13 (87.40) 11.87 (12.60)
[Co(HL ^b) ₂ (H ₂ O)(Cl)]	51-144 2.73 (3.26)	144-405 39.14 (40.44)	405-619 46.76 (45.46)	88.63 (89.16) 11.37 (10.84)
[Co(HL ^c) ₂ (H ₂ O)(Cl)]	67-162 2.63 (3.19)	162-396 41.28 (40.73)	396-644 45.12 (44.67)	89.03 (88.59) 10.97 (11.41)
[Co(HL ^d) ₂ (H ₂ O)(Cl)]	45-168 2.55 (3.04)	168-370 43.84 (44.49)	370-680 43.01 (41.52)	89.40 (89.05) 10.60 (10.95)
[Co(HL ^e) ₂ (H ₂ O)(Cl)]	40-140 2.48 (2.94)	140-426 44.83 (45.32)	426-627 42.39 (41.88)	89.70 (90.14) 10.30 (9.86)
[Co(HL ^f) ₂ (H ₂ O)(Cl)]	59-155 2.38 (2.81)	155-432 46.88 (47.61)	432-653 40.82 (39.21)	90.08 (89.63) 9.92 (10.37)

Table 5. Antimicrobial effects of the ligands and the Co(III) complexes^a.

Compounds	E.A. CCM 2531	P.A. DSM 50071	E.C. ATCC 25922	S.A. COWAN I	S.C. FMC 16	C.A. FMC 17	B.S.
H ₂ L ^a	12	—	—	—	—	—	—
H ₂ L ^b	—	—	—	—	10	—	12
H ₂ L ^c	13	15	—	14	13	17	13
H ₂ L ^d	14	—	—	11	21	12	11
H ₂ L ^e	14	15	15	13	15	13	14
H ₂ L ^f	14	—	—	11	25	12	11
[Co(HL ^a) ₂ (H ₂ O)(Cl)]	13	—	12	—	—	13	—
[Co(HL ^b) ₂ (H ₂ O)(Cl)]	—	11	11	—	10	—	—
[Co(HL ^c) ₂ (H ₂ O)(Cl)]	13	15	—	14	13	17	13
[Co(HL ^d) ₂ (H ₂ O)(Cl)]	15	14	14	17	13	16	13
[Co(HL ^e) ₂ (H ₂ O)(Cl)]	15	14	15	14	13	15	13
[Co(HL ^f) ₂ (H ₂ O)(Cl)]	17	15	12	13	17	14	15
Azm 15	25	24	21	24	24	24	23

^aCompound concentration = 100µg/disc; a: including disk diameter (9 mm). Azm 15: Azithromycin; symbol (-) reveals that the compounds had no activity against the microorganisms

The molar conductance values measured in DMSO solutions (*ca.* 1 x 10⁻³ M) for these mononuclear Co(III) complexes are in the 6.9-10.3 Ω⁻¹ cm² mol⁻¹ range. According to these results, the complexes are not electrolytes³¹.

The metal contents were determined by FAAS, and the TGA curves for the Co(III) complexes were obtained at a heating rate of 10 °C/min in a nitrogen atmosphere over the temperature range 25-800 °C. The decomposition temperature and the weight losses of the complexes were calculated from the TGA data. The decomposition of the Co(III) complexes starts around 38-67 °C and finishes around 619-680 °C. The Co(III) complexes decompose to CoO in 3 steps in the temperature ranges³². In the decomposition process of all the Co(III) complexes, the mass loss, corresponding to a water molecule, and weight loss were observed around 38-168 °C³³.

The bacterial and fungal activities of the complexes and *Azithromycin* were investigated against 7 different bacteria and fungi, mentioned above. The compounds were usually found less effective than *Azithromycin* against bacteria and fungi. All the complexes exhibited inhibition against some microorganisms. The results show that [Co(HL^d)₂(H₂O)(Cl)], [Co(HL^e)₂(H₂O)(Cl)] and [Co(HL^f)₂(H₂O)(Cl)] complexes have the highest antimicrobial activity. [Co(HL^a)₂(H₂O)(Cl)] and [Co(HL^b)₂(H₂O)(Cl)] complexes have the lowest antimicrobial activity against some microorganisms. H₂L^a is effective only on *Enterobacter aeruginosa* and H₂L^b was tested and found effective against *Saccharomyces cerevisiae* and *Bacillus subtilis niger*. The detailed biological activities data are given in Table 5. The compounds were the most active and may be considered promising for the development of new antifungal agents.

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