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Synthesis and Characterization of New (*E*,*E*)-dioximes and Their Divalent Metal Complexes[1]

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Abstract—Two new soluble vic-dioxime ligands, 4-isopropylanilineglyoxime (L^1H_2) and 4-benzylpiperidineglyoxime (L^2H_2) were prepared by reacting 4-isopropylaniline and 4-benzylpiperidine with *anti*-chloroglyoxime. Ten metal complexes were obtanied by reacting both ligands with Cu(II), Ni(II), Co(II), Zn(II), and Cd(II) cations. The ligands and their metal complexes were elucidated by elemental analysis, IR, UV-vis, ^{1}H NMR, and ^{13}C NMR and also magnetic moments of the complexes were determined.

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INTRODUCTION

vic-Dioxime complexes, which were synthesized for the first time by Tschugaev, have been the focus of a great deal of interest through the decades of never-ending series of interesting reports due to their similarity to vitamin B_{12} [1–5].The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure that is stabilized by hydrogen-bonded bridges [1].

The presence of slightly basic nitrogen atoms and mildy acidic hydroxyl groups make *vic*-dioximes amphoteric ligands, which form corrin-type, square-planar, square-pyramidal or octahedral complexes with transition metal ions such as Cu^{2+}, Ni^{2+}, Pd^{2+}, Co^{2+}, and Co^{3+} as central atoms [6, 7]. The stable complexes prepared with *vic*-dioxime ligands have been used for various purposes such as oxidation reagents, additive materials for the improvement of pigments, mechanic oils, epoxy resins and rubber, in industry, etc. [8]. Oxime metal complexes are utilized in medicine as well; Tc(V) and Cu(II) containing *vic*-dioximes currently are used as cerebral and myocardial perfusion imaging agents [9–11].

In the present study, we report the synthesis and characterization of novel soluble *vic*-dioxime ligands and their mononuclear complexes with Cu(II), Ni(II), Zn(II), Co(II), and Cd(II).

EXPERIMENTAL

Materials. 4-Isopropylaniline, 4-benzylpiperidine, all solvents, and all metal salts purchased from E. Merck were reagent grade and were used as received. Anti-chloroglyoxime was prepared by a reported procedure [12, 13].

Physical measurement. Elemental analyses of the synthesized compounds (C, H, N) were performed using a LECO-932 CHNSO model analyzer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR spectrometer (in DMSO-d_6). IR spectra were measured on a Perkin Elmer Model 1605 FT-IR spectrophotometer as KBr pellets. The UV-vis spectra were recorded on a Shimadzu 160 A spectrofotometer. Magnetic moments of the complexes were measured using a Sherwood Scientific Model MX1 Gouy magnetic susceptibility balance at room temperature using $Hg[Co(SCN)_4]$ as calibrate; diamagnetic corrections were calculated from Pascal's constants.

Synthesis of 4-isopropylanilineglyoxime (L^1H_2) and 4-benzylpiperidineglyoxime (L^2H_2). 4-isopropylaniline (1.4 ml, 5 mmol) or 4-benzylpiperidine (0.9 ml, 5 mmol) was dissolved in absolute ethanol (15 ml). A solution containing anti-chloroglyoxime (0.6 g, 5 mmol) in ethanol (5 ml) was added slowly at room temperature with constant stirring. The reaction mixture was stirred continuously for 1 h at room temperature. The pH of the mixture was about 7.0–7.5. Its volume was then doubled by adding distilled water. The precipitated ligands were filtered off, washed with cold water, dried and crystallized from water–ethanol (1 : 2).

The L^1H_2 and L^2H_2 ligands are soluble in common solvents, such as $CHCl_3$, EtOH, THF, DMSO and acetonitrile. ^{13}C NMR spectral data for L^1H_2 ($CDCl_3$, TMS, δ, ppm): C^1(23.94), C^2(33.48), C^3(135.75), C^4(127.18), C^5(122.50), C^6(145.82), C^7(145.08), C^8(141.78). ^{13}C NMR spectral data for L^2H_2 ($CDCl_3$, TMS, δ, ppm): C^1(124.24), C^2(126.18), C^3(125.94), C^4(138.70),

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[1] The text was submitted by the authors in English.

Table 1. Analytical and physical data for the ligands and their complexes

Compound	Molecular formula (F.W., g/mol)	Color	M.p., °C	Yield, %	Content (calcd/found), %		
					C	H	N
L^1H_2	$C_{11}H_{15}N_3O_2$ (221.25)	White	141	68	59.72/60.33)	6.82/6.25)	18.99/19.14)
$(L^1H)_2Ni$	$C_{22}H_{28}O_4N_6Ni$ (499.19)	Dark red	266*	60	52.93/53.01	5.65/5.70	12.82/13.10
$(L^1H)_2Cu$	$C_{22}H_{28}O_4N_6Cu$ (504.04)	Green	295	42	49.18/50.10	4.78/4.60	12.46/12.85
$(L^1H)_2Co \cdot 2H_2O$	$C_{22}H_{32}N_6O_6Co$ (535.46)	Brown	299	62	49.35/49.30	6.02/6.50	15.70/16.00
$(L^1H)Cl(H_2O)Cd$	$C_{11}H_{16}N_3O_3ClCd$ (388.80)	Yellow	172*	48	37.80/36.20	5.10/4.80	11.20/11.70
$(L^1H)Cl(H_2O)Zn$	$C_{11}H_{16}N_3O_3ClZn$ (339.12)	White	278	44	38.96/39.15	4.75/5.12	12.39/13.12
L^2H_2	$C_{14}H_{19}N_3O_2$ (261.31)	White	148	60	64.35/63.28	8.73/7.99	16.08/1580
$(L^2H)_2Ni$	$C_{28}H_{36}N_6O_4Ni$ (579.31)	Red	227	75	58.05/57.75	6.26/6.02	14.51/13.28
$(L^2H)_2Cu$	$C_{28}H_{36}N_6O_4Cu$ (584.35)	Dark green	178*	40	54.55/54.80	5.34/5.40	13.14/13.80
$(L^2H)_2Co \cdot 2H_2O$	$C_{28}H_{40}N_6O_6Co$ (615.56)	Brown	251	65	54.63/53.50	6.54/5.50	13.65/13.20
$(L^2H)Cl(H_2O)Cd$	$C_{14}H_{20}N_3O_3ClCd$ (426.19)	Yellow	161*	58	43.13/42.45	5.73/5.80	13.28/12.40
$(L^2H)Cl(H_2O)Zn$	$C_{14}H_{20}N_3O_3ClZn$ (379.18)	White	150	55	44.35/43.28	5.31/5.80	11.08/(12.12

* Decomposition point.

C^5(40.70), C^6(34.92), C^7(30.98), C^8(45.20), C^9(150.18), C^{10}(130.83).

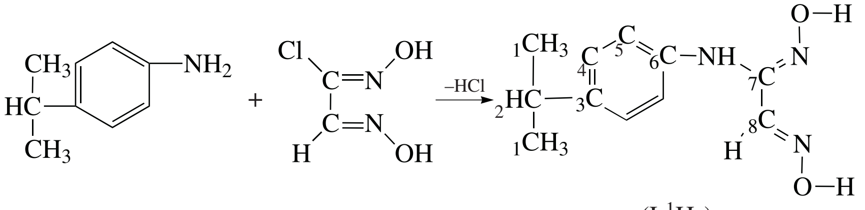
Table 1 gives analytical and physical data for the ligands. IR, ^1H NMR, and UV-vis spectra data of the ligands are given in tables 2–4, respectively.

Synthesis of the Ni(II), Co(II), and Cu(II) complexes with L^1H_2 and L^2H_2. A solution of the metal salt ($NiCl_2 \cdot 6H_2O$ (1.189 g, 5 mmol) or $CoCl_2 \cdot 6H_2O$ (1.190 g, 5 mmol) or $CuCl_2 \cdot 2H_2O$ (0.852 g, 5 mmol)) dissolved in H_2O (15 ml) was added dropwise to a stirred solution of the ligand (L^1H_2 (2.8 ml, 10 mmol) or L^2H_2 (1.8 ml, 10 mmol)) dissolved in EtOH (20 ml). The pH of the reaction mixture 3.5–4.0 was then adjusted to 5.5–6.0 by the addition of 1% NaOH in EtOH. The mixture was stirred on a water bath at 45–50°C for 1 h. The precipitates were filtered off, washed with cold water, and dried.

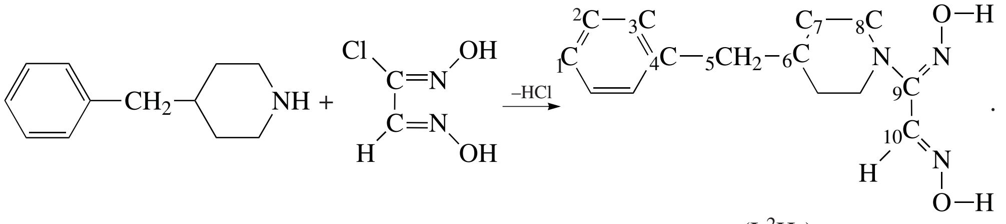
The Ni(II) complexes are soluble in DMSO, DMF, and $CHCl_3$. Spectral data for the Ni(II) complexes: ^{13}C NMR ($CDCl_3$, TMS, δ, ppm): C^1(24.10), C^2(39.61), C^3(132.61), C^4(127.63), C^5(123.82), C^6(148.10), C^7(145.80), C^8(136.35); ^{13}C NMR ($CDCl_3$, TMS, δ, ppm): C^1(127.20), C^2(126.10), C^3(130.24), C^4(136.72), C^5(40.68), C^6(36.20), C^7(30.80), C^8(43.20), C^9(150.16), C^{10}(128.62).

Synthesis of the Cd(II), Zn(II) complexes with L^1H_2 and L^2H_2. A solution of the metal salt ($CdCl_2 \cdot H_2O$ (1.005 g, 5 mmol) or $ZnCl_2$ (0.670 g, 5 mmol)) dissolved in H_2O (15 ml) was added dropwise to a stirred solution of the ligand (L^1H_2 (1.4 ml, 5 mmol) or L^2H_2 (0.9 ml, 5 mmol)). The pH of the reaction mixture 3.5–4.0 was then adjusted to 10.0–11.0 for Cd(II) complex and 7.0–7.5 for the Zn(II) complex by the addition of 1% NaOH in EtOH. The mixture was stirred on a water bath at 45–50°C for 1 h. The precipitates were filtered off, washed with cold water, and dried.

L^1H_2 and L^2H_2 were prepared by a one-step reaction between anti-chloroglyoxime and corresponding amines. The reactions of preparing of *vic*-dioxime ligands are given below:



(L^1H_2)



(L^2H_2)

RESULTS AND DISCUSSIONS

L^1H_2 and L^2H_2 are highly soluble in common organic solvents, such as EtOH, $CHCl_3$, acetonitrile, or DMSO. The results of elemental analysis of L^1H_2 and L^2H_2 are in agreement with theoretical expectations (Table 1). In the IR spectrum of the ligands (Table 2), an OH stretching vibration is observed at 3314 and 3238 cm^{-1}, respectively, as a broad absorption. The NH, C=N, and NO stretching vibrations are at 3400–3420, 1656–1659, and 990–970 cm^{-1}, respectively, as expected for the substituted aminoglyoximes [14–16].

In the ^1H NMR spectrum of L^1H_2 and L^2H_2 in DMSO-d_6 (Table 3) two peaks are observed for the protons, since the OH protons of the oxime groups are not equivalent [17–19]. The chemical shifts of =N–OH pro-

Table 2. Characteristic IR bands (cm^{-1}) of the ligands and complexes as KBr pellets

Compounds	ν(O–H)	ν(N–H)	ν(O···H–O)	ν(C=N)	ν(N–O)	Others
L^1H_2	3314	3400		1656	990	
$(L^1H)_2Ni$		3394	1770	1616	980	
$(L^1H)_2Cu$		3393	1760	1615	970	
$(L^1H)_2Co \cdot 2H_2O$		3392	1770	1618	976	3430 (H_2O)
$(L^1H)Cl(H_2O)Cd$	3305	3287		1630	956	
$(L^1H)Cl(H_2O)Zn$	3310	3160		1618	970	
L^2H_2	3238	3420		1659	970	
$(L^2H)_2Ni$		3415	1765	1620	960	
$(L^2H)_2Cu$		3412	1780	1618	955	
$(L^2H)_2Co \cdot 2H_2O$		3424	1800	1622	958	3450 (H_2O)
$(L^2H)Cl(H_2O)Cd$	3310	3340		1620	960	
$(L^2H)Cl(H_2O)Zn$	3310	3280		1630	950	

Table 3. ^1H NMR spectra of the ligands and their Ni(II) complexes in DMSO-d_6

Compound	O–H[a]	O–H[a]	$H_{Arom.}$	[a]HN–C=	=CH	O–H···O
L^1H_2	11.80	10.75	6.40–7.20	7.62	7.20	
$(L^1H)_2Ni$			6.20–7.15	7.60	7.18	15.20
L^2H_2	11.01	11.10	6.90–7.20		7.25	
$(L^2H)_2Ni$			6.80–7.20		7.25	16.10

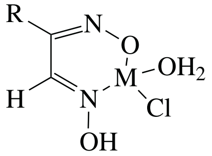
[a] Dissappears on D_2O exchange.

tons are observed at 11.80–10.75 ppm for L^1H_2 and 11.01–11.10 ppm for L^2H_2 as singlets. A single chemical shift for the OH proton indicates that the oxime groups prevail in the anti form [20]. In L^1H_2 the NH group appears as singlet at 7.62 ppm. These resonances disappear upon addition of D_2O to the solution. In these ligands the CH proton adjacent to the oxime group is observed at 7.20 and 7.25 ppm. More detailed information about the structure of the ligands is provided by ^{13}C NMR spectral data. In the ^{13}C NMR spectrum, the carbon resonances of oxime groups are observed at 145.08 and 141.78 ppm for L^1H_2 and 150.18 and 130.83 ppm for L^2H_2. Observation of dioxime carbons in the ^{13}C NMR spectra at two different frequencies indicates that the *vic*-dioxime ligands have the *anti* structure [21].

The synthesis of the mononuclear complexes was achieved at room temperatures. The results of elemental analysis of the complexes are in agreement with theoretical expectations (Table 1). *vic*-Dioxime derivatives L^1H_2 and L^2H_2 form probably square planar complexes with Ni(II), Cu(II) and octahedral complexes with Co(II) with a metal: ligand ratio of 1 : 2. The Cd(II) and Zn(II) complexes of these ligands are with a metal: ligand ratio of 1 : 1. In the IR spectra of the complexes (Table 2) C=N and NO stretching vibrations are observed at around 1615–1622 and 955–980 cm^{-1}, respectively. The C=N vibration is at lower frequency than for the free ligands, attributable to N,N-chelation [22, 23]. Weak bending vibrations of the O–H···O bridges are observed around 1660–1800 cm^{-1}. Disappearance of the stretching vibrations of the O–H band present in the free ligands is further evidence for O–H···O bond formation [24]. For the Co(II) complexes, coordinated H_2O molecules are identified by a broad OH absorption around 3430–3450 cm^{-1}.

In the IR spectrum of the Zn(II) and Cd(II) complexes the stretching band of ν(C=N) appeared around 1618–1630 cm^{-1} is shifted to 1656 cm^{-1} in L^1H_2 and 1659 cm^{-1} in L^2H_2. There is no (O···H–O) peak, as expected for these complexes. At the same time, the N–O band appearing around 990–960 cm^{-1} in the free ligands moved to lower frequency by ~20 cm^{-1} after Zn(II) and Cd(II) complex formation. These results suggest that the ligand is coordinated to each metal ion through nitrogen and oxygen donors. A chloride ion and water molecule are probably coordinated to each metal ions as reported for the Zn(II) and Cd(II) complexes of *vic*-dioximes [25–28].

The magnetic moments of the complexes, measured at room temperature, support the structure for the complexes (Table 4). The Co(II) and Cu(II) complexes are paramagnetic, whereas the Ni(II), Cd(II), and Zn(II) complexes are diamagnetic. Magnetic moments are 4.04, 3.81 μ_B (for Co(II) complexes) and 1.69, 1.89 μ_B (for Cu(II) complexes). The suggested structures of the Cd(II) and Zn(II) complexes are shown below:



(M = Cd(II), Zn(II); R = C_9H_{12} for L^1H_2
R = $C_{12}H_{16}$ for L^2H_2).

Table 4. Magnetic moments and characteristic UV-vis bands of the ligands and complexes

Compound	$\mu_{eff/atom}$, μ_B	λ_{max} , nm*
L^1H_2		301
$(L^1H)_2Ni$	Dia**	324, 434, 476, 690
$(L^1H)_2Cu$	1.69	300, 660, 670
$(L^1H)_2Co \cdot 2H_2O$	3.81	303, 635
$(L^1H)Cl(H_2O)Cd$	Dia	300, 610
$(L^1H)Cl(H_2O)Zn$	Dia	289, 310, 691
L^2H_2		230, 260
$(L^2H)_2Ni$	Dia	252, 325, 440, 680
$(L^2H)_2Cu$	1.89	269, 328, 550, 670
$(L^2H)_2Co \cdot 2H_2O)$	4.04	270, 350, 480
$(L^2H)Cl(H_2O)Cd$	Dia	280, 570
$(L^2H)Cl(H_2O)Zn$	Dia	270, 300, 420

Notes: * In DMF.
** Diamagnetic.

The UV-vis spectra of the ligands and complexes in DMF showed absorption bands between 230–690 nm. In the complexes the low intensity bands in the range 550–690 nm are consistent with $d \longrightarrow d$ transitions of the metal ions. The 250–380 nm bands correspond to both the $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ transitions of C=N and charge-transfer transition arised from π-electron interactions between the metal and ligand [29, 30].

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