SYNTHESIS AND CHARACTERIZATION OF 4-ARYLAMINOBI-PHENYLGLYOXIMES AND THEIR COMPLEXES

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ABSTRACT

4-Chloroacetyl biphenyl has been synthesized by Friedel-Crafts reaction between biphenyl and chloroacetyl chloride in the presence of AlCl_3 catalyst. The nitrosation reaction of this compound gave 4-biphenylhydroxamyl chloride (HL). Subsequently, 4-biphenylchloroglyoxime (H_2L) was prepared by the reaction of 4-biphenylhydroxamyl chloride and hydroxylamine hydrochloride. Then, six new substituted 4-biphenylaminoglyoximes (H_2L^x) have been synthesized from 4-biphenylchloroglyoxime and the corresponding amines. A series of $\text{M}(\text{II})$ -dioxime complexes of the type $[\text{M}(\text{HL}^x)_2]$ or $[\text{M}(\text{HL}^x)_2(\text{H}_2\text{O})_2]$ [$\text{M}(\text{II})=\text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$] have been synthesized and characterized by FT-IR, ^1H NMR spectral studies, elemental analysis, AAS and magnetic susceptibility measurements.

Keywords: Dioximes, Magnetic Properties, Metal Complexes, FT-IR

INTRODUCTION

Oximes are becoming increasingly important as analytical, biochemical and antimicrobial reagents and, in addition, they have received much attention due to their use as liquid crystals and dyes. The oximes of various types, such as α -dioximes, α -keto oximes, amino oximes etc. generally form coloured soluble or very slightly soluble chelates with some transition metal salts, which can be used for different analytical purposes¹⁻⁴. In recent years, dioxime ligands and complexes have been extensively studied since these structural units are thought to be involved in a variety of biochemical and industrial processes^{5,6}.

The stability of the *vic*-dioxime metal complex is due to the formation of hydrogen bonds between oximes with the release of one hydrogen atom per mole of oxime. As a result, two hydrogen atoms are released to the medium for each metal ion.

In a previous paper⁷, the formation of polymeric metal complexes with substituted bis(aminophenylglyoxime)methanes was studied. The number of new oxime ligands designed and synthesized has increased significantly and their structures have become interestingly complex⁸⁻¹⁰. In this paper, the synthesis and characterization of new dioxime ligands and their $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ complexes are described.

EXPERIMENTAL SECTION

Materials and methods

All chemicals were purchased from Merck and Fluka, and used without further purification.

^1H NMR spectra of ligands were obtained by the Laboratories of the Scientific and Technical research Council of Turkey (TUBITAK). IR spectra were recorded in KBr pellets in the $4000\text{--}400\text{ cm}^{-1}$ region using a Perkin Elmer Spectrum BX FT-IR spectrometer. The elemental analyses of all complexes and ligands were obtained using a LECO CHNS 932 Analyzer. Metal contents were determined using a Perkin Elmer AA 800 spectrometer. The room temperature magnetic susceptibility measurements were made by a Sherwood Scientific MX1 Gouy Magnetic Susceptibility Balance.

Synthesis

The synthetic pathway of these new ligands are illustrated in Figure 1. 4-Chloroacetyl biphenyl was synthesized according to the literature¹¹ from chloroacetyl chloride and biphenyl in the presence of AlCl_3 as catalyst in a Friedel-Crafts reaction. 4-Biphenylhydroxamyl chloride was prepared similar to method reported in the literature¹¹. A quantity of 2.3 g (10 mmol) 4-chloroacetyl biphenyl was dissolved in 50 mL chloroform with cooling, then passing HCl gas into the solution for half an hour and then 1.5 mL (11 mmol) butyl nitrite was added dropwise to the mixture with stirring and passing HCl gas into the mixture. The mixture was left overnight at room temperature to form a precipitate. The precipitate was filtered and recrystallized from ether-hexane (1:1). The crystallized product was filtered, washed with hexane and dried.

Figure 1- The synthetic pathway of ligands($x=1\text{--}6$)

4-Biphenylchloroglyoxime; A quantity of 2.60 g (10 mmol) 4-biphenylhydroxamyl chloride was dissolved in 25 mL ethanol. Subsequently, solution of 0.76 g (11 mmol) $\text{NH}_2\text{OH}.\text{HCl}$ (dissolved in the minimum amount of water) were added with stirring. The reaction mixture was heated for 5 h at 50°C and then the mixture left stand for four days. The precipitate was filtered and recrystallized from ethanol.

The substituted 4-biphenylaminoglyoximes; have been obtained by the reaction of amines (22 mmol, aniline, benzylamine, *p*-toluidine, 4-chloroaniline, 4-aminoacetophenone and pyrrolidine) with 4-biphenylchloroglyoxime (20 mmol, 0.55 g) in the presence triethylamine (22 mmol). The amine and triethylamine dissolved in 10 mL methanol were added dropwise to a suspension of 4-biphenylchloroglyoxime in 50 mL methanol over 15 min. The mixture was stirred further for 5-6 h, then diluted 100 mL water. The resulting precipitates were filtered and then recrystallized from ethanol-water (1:4). The product were filtered, washed with water and dried.

Synthesis of the $\text{Co}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$ Complexes; A quantity of 1.00 mmol substituted 4-biphenylaminoglyoxime was dissolved in 20 mL ethanol. Then the solution of 0.50 mmol $\text{Co}(\text{NO}_3)_2.6\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2.\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2.4\text{H}_2\text{O}$ in 20 mL ethanol (95 %) was added dropwise with stirring. The pH of the reaction mixture was around 3.5-4.0 and then was adjusted to 5.5-6.0 by adding 1% KOH solution. The complex precipitated was kept on a water bath at 80°C for one hour in order to complete the precipitation. The precipitate was filtered, washed with water, ethanol and ether and dried.

RESULTS AND DISCUSSION

NMR Spectra: The structures of the starting compounds and dioximes were identified by a combination of elemental analyses, ^1H NMR and IR spectra. In the ^1H NMR spectra of the 4-biphenylhydroxamyl chloride, a singlet at $\delta=13.69$ ppm correspond to the $=\text{N}-\text{OH}$ proton. ^1H NMR spectrum of 4-biphenylchloroglyoxime in DMSO clearly demonstrates the presence of a two $=\text{N}-\text{OH}$ environment at 12.51 and 12.70 ppm. When the chemical shifts

values of the two OH groups in the substituted 4-biphenylaminoglyoximes are compared, the ones at lower field quite closely resemble each other (11.74-11.85 ppm) while a considerable difference was observed for the ones at the higher field (8.87-11.49 ppm). The appearance of new signals at 8.04-8.80 ppm in the ligands with integration corresponding to one proton except H_2L^6 can be

assigned to coordination of the ammine group. The aromatic C-H protons were observed at 6.56-8.28 ppm, the aliphatic C-H protons at 2.17-3.89 ppm and CH protons of pyrrolidine ring at 2.78-3.88 ppm, respectively. These values are in good agreement with those of *vic*-dioximes¹² (Table I).

Table 1. The 1H NMR data (as p.p.m.) for the ligands

Compound	O-H ^a	O-H ^b	C-H _(arom.)	C-H _(alif.)	N-H
HL	13.69(s, 1H)	-	7.31-8.08(m, 9H)	-	-
H_2L	12.51(s, 1H)	12.70(s, 1H)	7.24-7.90(m, 9H)	-	-
H_2L^1	11.49(s, 1H)	11.83 (s, 1H)	6.56-8.12(m,14H)	-	8.46(s, 1H)
H_2L^2	10.00 (s, 1H)	11.74(s, 1H)	7.20-7.89(m,14H)	3.89 (d, 2H)	8.04(t, 1H)
H_2L^3	10.55(s, 1H)	11.80(s, 1H)	6.71-8.18(m,13H)	2.17 (s, 3H)	8.62(s, 1H)
H_2L^4	10.64(s, 1H)	11.80(s, 1H)	6.79-8.28(m,13H)	-	8.73(s, 1H)
H_2L^5	11.09(s, 1H)	11.85(s, 1H)	6.94-7.93(m,13H)	2.45(s, 3H)	8.80(s, 1H)
H_2L^6	8.87 (s, 1H)	11.76(s, 1H)	7.37-7.90(m,13H)	2.78-3.88	-

a; the first OH of oxime group , b; the second OH of oxime group
s; singlet, d; doublet, t; triplet, m; multiplet

The M(II) complexes of the substituted 4-biphenylaminoglyoximes were obtained in ethanol by the addition of sufficient 1 % KOH to increase the pH to 5.5-6.0. The experimental data obtained in this investigation establish that the reactions of dioximes with metal ions can be described by the following equation:

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

H_2L^1 = 4-Phenylaminobiphenylglyoxime, $[C_{20}H_{17}N_3O_2]$

H_2L^2 = 4-Benzylaminobiphenylglyoxime, $[C_{21}H_{19}N_3O_2]$

H_2L^3 = 4-(4-Methylphenylamino)biphenylglyoxime, $[C_{22}H_{19}N_3O_2]$

H_2L^4 = 4-(4-Chlorophenylamino)biphenylglyoxime, $[C_{20}H_{16}N_3O_2Cl]$

H_2L^5 = 4-(4-Acetylphenylamino)biphenylglyoxime, $[C_{22}H_{19}N_3O_3]$

H_2L^6 = 4- Pyrrolidylbiphenylglyoxime, $[C_{18}H_{19}N_3O_2]$

The structure of complexes are shown in Figure 2 and their colors, melting points, elemental analysis results are given in Table 2 and FT-IR data and magnetic measurement are given in Table 3. The structure of complexes were characterised by IR, elemental analyses and magnetic measurements. Analytical data for complexes (Table 2) agree with proposed molecular formula. 1H NMR spectra of these complexes could not be taken because of their very low solubility in organic solvents.

IR Spectra: The IR spectra of the free ligand were compared with those of the metal complexes in order to ascertain the bonding mode of the ligand to the metal ion in the complexes. The IR spectra of the HL showed very strong bands in the 1656 cm^{-1} , characteristic of the carbonyl stretching vibration. The former band has completely disappeared in the IR spectra of H_2L . The stretching vibrations of -NH- in the ligands, observed at $3357\text{-}3371\text{ cm}^{-1}$, remained unattacked in all the complexes ($3342\text{-}3401\text{ cm}^{-1}$) indicating that neither of the nitrogen atoms of ammine group are involved in chelating. In general, the complexes exhibited very similar IR features. This is indirect evidence that the complexes are of similar structures. As in the case of $[M(HL^x)_2]$ or $[M(HL^x)_2(H_2O)_2]$ [M=Co(II), Cu(II) and Ni(II)], the frequencies ν_{O-H} of the free oximes are shifted from $3236\text{-}3184\text{ cm}^{-1}$ to $2300\text{-}2400\text{ cm}^{-1}$ indicating strong intramolecular O-H...O hydrogen-bonding, which stabilizes the co-planar moiety in the octahedral and square-planar structure. The C=N bands of the free dioximes appear at $1607\text{-}1643\text{ cm}^{-1}$, suffer a positive shift of $30\text{-}40\text{ cm}^{-1}$ in the complexes suggesting involvement of the nitrogen atom of oxime group in the chelating with the metal ion¹⁷⁻¹⁸. In the FT-IR spectra of ligands, bands at $935\text{-}958\text{ cm}^{-1}$, was assigned to NO stretching vibrations. In the IR spectra of the complex, a shift of the vibration corresponding to the N-O band to higher frequency also indicates the formation of coordination bonds between metal and nitrogen atoms of the oximes. These values are in good agreement with those of *vic*-dioximes^{4,13,15,19,20}.

The elemental analyses of the complexes indicates that the metal-ligand ratio are 1:2 in the all metal complexes. According to the FT-IR data, elemental

analyses results and magnetic susceptibility measurements, the Cu(II), Ni(II) and Co(II) complexes have an octahedral structure, except the Ni(II) complexes of H_2L^2 , H_2L^3 and H_2L^6 , which are square-planar. Magnetic susceptibility measurements of the complexes provide information regarding their structures and are shown in Table 2. The Ni(II) complexes are diamagnetic except the octahedral Ni(II) complexes. This octahedral Ni(II) complexes are paramagnetic with a magnetic susceptibility values of $2.35\text{-}3.73\text{ B.M.}$, which is in agreement with the two-spin value of 2.83 B.M. . According to the elemental analyses and Atomic Absorption Spectrometry(AAS) results also these Ni(II) complexes have an octahedral structure. The magnetic data of the Ni(II) complexes agree with a d^8 metal ion in a square-planar field or an octahedral configuration.

The Cu(II) and Co(II) complexes are paramagnetic with magnetic susceptibility values of $1.38\text{-}2.06$ and $3.52\text{-}4.66\text{ B.M.}$, respectively. This values are in agreement with a spin value of 1.73 B.M. and three-spin value of 3.87 B.M. to Cu(II) and Co(II) complexes, respectively²¹. The results are all in good agreement with the proposed structures for the obtained complexes.

should be replaced by

M=M(II) or M(II).2H₂O [M=Co, Cu, Ni]

Figure 2- The Structure of Complexes

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

Compound	Colour	Mp (°C)	Yield (%)	Calcd.(Found) %			
				C	H	N	Metal
HL	Light yellow	170	70	64.74(63.62)	3.85(3.24)	5.39(5.34)	-
H ₂ L	Cream	196	47	61.20(61.99)	4.01(3.68)	10.20(9.34)	-
H ₂ L ¹	Cream	62	71	72.51(72.28)	5.14(5.26)	12.69(12.31)	-
[Co(HL ¹) ₂ (H ₂ O) ₂]	Dark green	294*	95	63.58(63.45)	4.77(4.34)	11.13(10.78)	7.81(8.22)
[Cu(HL ¹) ₂ (H ₂ O) ₂]	Dark brown	239*	98	63.20(62.85)	4.74(4.54)	11.06(10.88)	8.37 (8.16)
[Ni (HL ¹) ₂ (H ₂ O) ₂]	Dark brown	275*	85	63.60(63.11)	4.77(4.30)	11.13(11.01)	7.78 (7.49)
H ₂ L ²	Light yellow	74	92	73.03(72.62)	5.51(5.42)	12.17(11.85)	-
[Co(HL ²) ₂ (H ₂ O) ₂]	Dark green	231*	96	64.37(63.99)	5.11(4.84)	10.73(10.47)	7.52 (8.43)
[Cu(HL ²) ₂ (H ₂ O) ₂]	Dark brown	186*	93	64.00(63.81)	5.08(4.75)	10.67(10.32)	8.07 (8.40)
[Ni(HL ²) ₂]	Red	196*	91	67.50(67.41)	4.82(4.54)	11.25(11.04)	7.86 (7.55)
H ₂ L ³	Light brown	89	54	73.04(72.83)	5.51(5.62)	12.17(10.84)	-
[Co(HL ³) ₂ (H ₂ O) ₂]	Dark green	290*	62	64.37(64.11)	5.11(4.94)	10.73(10.64)	7.52 (7.39)
[Cu(HL ³) ₂ (H ₂ O) ₂]	Dark brown	264*	71	64.00(63.69)	5.08(5.40)	10.67(10.74)	8.07 (8.12)
[Ni(HL ³) ₂]	Red	297*	61	67.50(67.77)	4.82(4.85)	11.24(11.03)	7.86 (7.89)
H ₂ L ⁴	Yellow	85	73	65.66(66.17)	4.38(4.59)	11.49(11.15)	-
[Co(HL ⁴) ₂ (H ₂ O) ₂]	Brown	300*	88	58.26(57.92)	4.13(4.07)	10.20 (9.87)	7.15 (7.58)
[Cu(HL ⁴) ₂ (H ₂ O) ₂]	Dark brown	234*	94	57.93(57.81)	4.10(3.96)	10.14 (9.78)	7.67 (7.45)
[Ni(HL ⁴) ₂ (H ₂ O) ₂]	Dark green	290*	80	58.27(58.04)	4.13(3.77)	10.20 (9.91)	7.13 (7.48)
H ₂ L ⁵	Yellow	177	72	70.78(70.33)	5.09(5.36)	11.26(10.94)	-
[Co(HL ⁵) ₂ (H ₂ O) ₂]	Dark brown	287*	88	62.94(62.88)	4.77(4.34)	10.01 (9.85)	7.02 (7.44)
[Cu(HL ⁵) ₂ (H ₂ O) ₂]	Dark brown	249*	92	62.52(62.11)	4.74(4.57)	9.95 (9.68)	7.52 (7.29)
[Ni(HL ⁵) ₂ (H ₂ O) ₂]	Brown	294*	68	62.96(62.69)	4.77(4.36)	10.02 (8.69)	7.00 (7.18)
H ₂ L ⁶	Yellow	75	88	69.90(69.77)	6.15(6.56)	13.59(13.95)	-
[Co(HL ⁶) ₂ (H ₂ O) ₂]	Brown	235*	60	60.77(60.57)	5.63(5.29)	11.82(10.97)	8.29 (8.51)
[Cu(HL ⁶) ₂ (H ₂ O) ₂]	Green	194*	72	60.37(60.29)	5.59(5.23)	11.74(11.48)	8.88 (8.65)
[Ni(HL ⁶) ₂]	Dark red	278*	77	64.03(64.49)	5.34(5.29)	12.45(11.97)	8.70 (8.38)

*Decomposition point

Table 3. Magnetic measurements and IR spectral data for the ligands and their metal complexes (cm⁻¹)

Compounds	μ_{eff} (B.M.)	N-H	$\nu(\text{OH})$	$\nu(\text{CH})_{\text{alip}}$	$\nu(\text{O-H}\cdots\text{H})$	$\nu(\text{C=N})$	$\nu(\text{NO})$
HL	-	-	3260 b	2919 w	-	1602 s	1029 s
H ₂ L	-	-	3272 b	2908 w	-	1601 s	988 s
H ₂ L ¹	-	3371 m	3198 b	2890 w	-	1632 s	954 s
[Co(HL ¹) ₂ (H ₂ O) ₂]	3.52	3377 m	-	2930 w	2361 w	1599s	1007 m
[Cu(HL ¹) ₂ (H ₂ O) ₂]	1.65	3378 m	-	2922 w	2360 w	1598 s	1007 m
[Ni(HL ¹) ₂ (H ₂ O) ₂]	2.35	3343 m	-	2925 w	2360 w	1596 s	1006 m
H ₂ L ²	-	3361 w	3184 b	2928 w	2362 m	1634 s	955 s
[Co(HL ²) ₂ (H ₂ O) ₂]	3.52	3399 m	-	2927 w	2361 w	1599 s	1007 m
[Cu(HL ²) ₂ (H ₂ O) ₂]	1.47	3401 m	-	2924 w	2359 w	1602 s	1007 m
[Ni(HL ²) ₂]	Dia.	3401 m	-	2941 w	2360 m	1597 s	1006 m
H ₂ L ³	-	3360 w	3185 b	2922 w	2362 m	1635 s	955 s
[Co(HL ³) ₂ (H ₂ O) ₂]	4.66	3379 b	-	2920 w	2361 w	1597 s	1007 m
[Cu(HL ³) ₂ (H ₂ O) ₂]	1.38	3350 b	-	2920 w	2362 m	1507 s	1007 m
[Ni(HL ³) ₂]	Dia.	3342 b	-	2924 w	2360 m	1593 s	1006 s
H ₂ L ⁴	-	3357 m	3201 b	2894 w	2361 m	1633 s	949 s
[Co(HL ⁴) ₂ (H ₂ O) ₂]	4.31	3369 m	-	2928 w	2361 m	1597 s	1008 m
[Cu(HL ⁴) ₂ (H ₂ O) ₂]	1.97	3382 m	-	2926 w	2361 m	1599 s	1008 m
[Ni(HL ⁴) ₂ (H ₂ O) ₂]	3.32	3381 m	-	2929 w	2360 m	1597 s	1008 m
H ₂ L ⁵	-	3360 m	3193 b	2894 w	2360 m	1643 s	958 s
[Co(HL ⁵) ₂ (H ₂ O) ₂]	4.44	3370 m	-	2929 w	2364 w	1596 s	1008 m
[Cu(HL ⁵) ₂ (H ₂ O) ₂]	1.78	3382 m	-	2922 w	2362 w	1596 s	1007 m
[Ni(HL ⁵) ₂ (H ₂ O) ₂]	3.73	3368 m	-	2922 w	2359 w	1596 s	1007 m
H ₂ L ⁶	-	-	3236 b	2970 w	2361 m	1607 s	935 s
[Co(HL ⁶) ₂ (H ₂ O) ₂]	3.75	-	3369 b	2969 w	2360 m	1551 s	1007 m
[Cu(HL ⁶) ₂ (H ₂ O) ₂]	2.06	-	3411 b	2969 w	2361 m	1570 s	1007 m
[Ni(HL ⁶) ₂]	Dia.	-	3447 b	2965 w	2362 m	1558 s	1006 m

s: strong, m: medium, w:weak, b:broad

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