Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

The Synthesis of Biphenylglyoxime and Bis(Phenylglyoxime) and Their Complexes with Cu(II), Ni(II) and Co(II)

Ibrahim Karataş [a] & H. Ismet Uçan [a]

[a] Department of Chemistry , Faculty of Arts and Sciences University of Selçuk , 42079, Konya, Turkey

To cite this article: Ibrahim Karataş & H. Ismet Uçan (1998) The Synthesis of Biphenylglyoxime and Bis(Phenylglyoxime) and Their Complexes with Cu(II), Ni(II) and Co(II), Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 28:3, 383-391, DOI: 10.1080/00945719809349362

To link to this article: http://dx.doi.org/10.1080/00945719809349362

SYNTH. REACT. INORG. MET.-ORG. CHEM., 28(3), 383–391 (1998)

THE SYNTHESIS OF BIPHENYLGLYOXIME AND BIS(PHENYLGLYOXIME) AND THEIR COMPLEXES WITH Cu(II), Ni(II) AND Co(II)

İbrahim Karataş* and H. İsmet Uçan

Department of Chemistry, Faculty of Arts and Sciences
University of Selçuk, 42079 Konya, Turkey

ABSTRACT

In this study, 4-acetylbiphenyl and 4,4'-diacetylbiphenyl have been synthesized from biphenyl. Their keto oximes and glyoximes derivatives have also been obtained. The metal complexes of the glyoximes such as copper, nickel and cobalt were prepared. The elemental analyses, FT-IR and ^{1}H NMR spectroscopy techniques were used to characterize the oximes and their complexes.

INTRODUCTION

vic-Dioximes and their derivatives are a very important class of ligands, forming complexes with transition metals. The complex of these compounds were begun first by Tschugaev in 1907 and have increased up to now[1-6]. Some oximes are widely used for various purposes in organic, analytical, inorganic, bio and industrial chemistry[7]. Oximes are used as additive materials for the improvement of pigments, mechanic oils, epoxy resins and rubber, in industry, etc.[8] Recently, some oximes and their alkyl, oxyalkyl and amino derivatives were proved to have physiological and biological activity[9-11].

In this work, the glyoximes of 4-acetylbiphenyl and 4,4'-diacetylbiphenyl and their metal complexes have been synthesized, extending our previous work, and the objective was to add new complexes to the literature of coordination chemistry.

The structures of the keto oximes and dioximes (ligands) synthesized from acetylbiphenyl and diacetylbiphenyl are shown in Fig. 1.

RESULTS AND DISCUSSION

In this study, 4-acetylbiphenyl and 4,4'-diacetylbiphenyl have been obtained by the reaction of acetylchloride with biphenyl in the presence of $AlCl_3$ catalyst according to the Friedel Crafts reaction[12-14]. Keto oximes (isonitrosooximes) and dioximes of these compounds have also been originally synthesized by following the literature[3,4]. The structures of these compopunds were identified by elemental analyses, ^1H NMR and FT-IR, as shown in Tables I, II and III.

In the ^1H NMR spectra of the oximes, two peaks are present for the OH protons of the dioxime groups (H_2L' and H_4L'') while the OH protons of the keto oximes (HL and H_2L) appear as singlet peaks. When the chemical shift values of the two OH groups in the dioximes are compared, the ones at lower field quite closely resemble each other (11.95-11.90 ppm) while a considerable difference is observed for the ones at the higher field (11.45-11.20 ppm)[4,5] (Table II).

The chemical shifts of the C-H protons adjacent to the oxime groups and the aromatic protons are at 8.50-8.15 ppm and 8.10-7.30 ppm, respectively. All these values are in agreement with the chemical shift values of oximes protons[15,16].

FT-IR data for characterising the structure of the ligands and their complexes are given in Table III. In the IR spectra of the oximes, O-H stretching vibrations appear as a broad absorption at 3280-3240 cm^{-1}. Bands due to C=N and N-O stretches appear at 1690-1610 cm^{-1}, and 1015-970 cm^{-1}, respectively; these absorption data are in agreement with those previously reported for other oximes derivatives[17,18]. Bands appearing at 2380-2370 cm^{-1} in the keto oximes and dioximes indicate that there are intermolecular H-bridges.

The Cu(II), Ni(II) and Co(II) complexes of the oximes were obtained in ethanol-water (1:1) mixture by the addition of sufficient 1 % NaOH to increase the

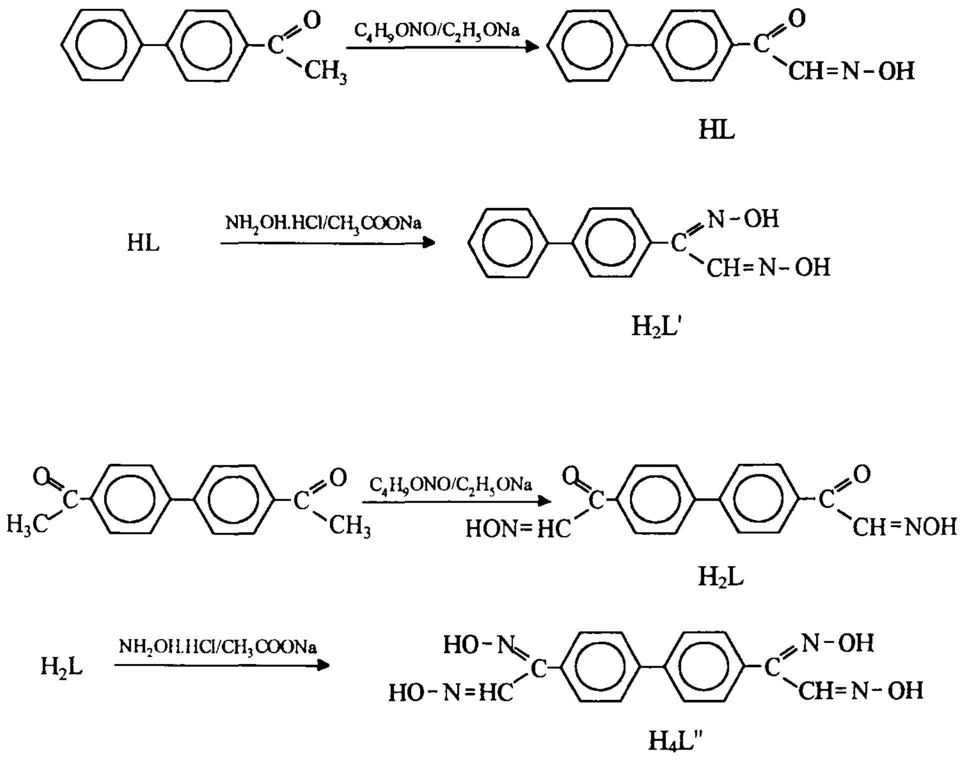

Fig. 1. The Structures of the Keto Oximes and Dioximes (Ligands)

pH to 5-5.5. Some physical properties of complexes are given in Tables I and III. The structures of the complexes were characterized by IR and elemental analyses. ^1H NMR spectra of the complexes could not be taken because of their very low solubility in organic solvents. In the IR spectra of the complexes, the shifts of the C=N stretching frequency to lower frequency and the vibration corresponding to the N-O band to higher frequency indicate the formation of coordination bonds between metal and the nitrogen atoms of the dioximes. The weak bands appearing around 1730-1710 cm^{-1} in the IR spectra of the complexes correspond to intermolecular hydrogen bridges (O-H...O), but these peaks are missing in the ligands. In addition, the broad

Table I. Some Physical Properties and Elemental Analytical Results of the Oximes and Their Complexes

Compound	Color	M.P. (°C)	Yield (%)	Formula Weights	Calculated (Found) % of C	H	N
HL	white	130-132	70	225.25	74.65	4.92	6.22
$[C_{14}H_{11}NO_2]$					(74.08)	(5.12)	(5.85)
H_2L'	light white	194-196	95	240.27	69.99	5.03	11.66
$[C_{14}H_{12}N_2O_2]$					(70.46)	(4.82)	(11.24)
H_2L	pale white	268-270	57	296.29	64.86	4.08	9.46
$[C_{16}H_{12}N_2O_4]$					(65.20)	(4.26)	(9.73)
H_4L''	light	277-278	80	326.32	58.89	4.32	17.17
$[C_{16}H_{14}N_4O_4]$	yellow				(58.47)	(4.56)	(16.88)
$(HL')_2Cu$	dark green	>300	88	542.06	62.04	4.09	10.34
$[(C_{14}H_{11}N_2O_2)_2Cu]$					(61.67)	(4.23)	(10.61)
$(HL')_2Ni$	red	>300	90	537.27	62.60	4.13	10.43
$[(C_{14}H_{11}N_2O_2)Ni]$					(63.02)	(4.30)	(10.15)
$(HL')_2Co(H_2O)_2$	dark	>300	90	573.49	58.64	4.57	9.77
$[(C_{14}H_{11}N_2O_2)Co(H_2O)_2]$	brown				(58.21)	(4.85)	(9.40)
$[(H_2L'')Cu]_n$	dark green	>300	82	$(387.84)_n$	49.55	3.12	14.45
$[C_{16}H_{12}N_4O_4Cu]_n$					(50.07)	(3.34)	(14.09)
$[(H_2L'')Ni]_n$	red	>300	85	$(383.05)_n$	50.18	3.16	14.63
$[C_{16}H_{12}N_4O_4Ni]_n$					(50.46)	(3.36)	(14.30)
$[(H_2L'')Co(H_2O)_2]_n$	dark	>300	86	$(419.28)_n$	45.84	3.85	13.36
$[C_{16}H_{12}N_4O_4Co.2H_2O]_n$	brown				(45.46)	(4.04)	(13.02)

Table II. ^1H NMR Data for the Oximes in DMSO-d_6 [δ(ppm)]

Compound	O-H[a]	O-H[a]	C-H(arom.)	C-H(aliph.)
HL	11.40	-	7.70-7.30	8.15
	(1H, s)		(9H, m)	(1H, s)
H_2L'	11.90-11.45	11.45	7.90-7.40	8.45
	(1H, s)	(1H, s)	(9H, m)	(1H, s)
H_2L	12.60	-	8.10-7.90	8.40
	(2H, s)		(8H, m)	(2H, s)
H_4L''	11.95	11.20	8.05-7.45	8.50
	(2H, m)	(2H, m)	(8H, m)	(2H, s)

a: Disappears on D_2O exchange, s: singlet, m: multiplet

Table III. Characteristic IR Bands of the Oximes and Their Complexes as KBr Pellets (cm^{-1})

Compound	ν(O-H)	ν(C-H) (arom)	ν(C-H) (aliph.)	ν(O-H...O) chelate	ν(C=N)	ν(N-O)	δ(O-H...O)
HL	3240	3030	2875	2370	1630	1015	-
H_2L'	3250	3020	2900	2375	1690	970	-
H_2L	3250	3030	2875	2380	1610	1010	-
H_4L''	3280	3020	2870	2370	1690	980	-
$(HL')_2Cu$	-	3010	2800	-	1650	980	1710
$(HL')_2Ni$	-	3020	2920	-	1660	990	1720
$(HL')_2Co(H_2O)_2$	3240	3040	2930	-	1640	1010	1730
$[(H_2L'')Cu]_n$	-	3020	2910	-	1640	990	1715
$[(H_2L'')Ni]_n$	-	3030	2930	-	1660	980	1710
$[(H_2L'')Co(H_2O)_2]_n$	3380	3050	2940	-	1650	1010	1720

Keto oxime

Dioxime

Fig. 2. The Hydrogen Bridges in the Keto Oximes and Dioximes

peaks appearing around 3450-3380 cm^{-1} in the Co(II) complexes indicate that H_2O is coordinated to Co(II).

When the elemental analyses of the complexes were investigated, the metal-ligand ratios were found to be 1:2 in the complexes of biphenylglyoxime and 1:1 in the polymeric complexes of bis(phenylglyoxime). The molecular weights of polymeric metal complexes of bis(phenylglyoxime) could not be determined because of their insolubility in organic solvents. According to the FT-IR data and elemental analysis results the Ni(II) and Cu(II) complexes have a square-planar structure, whereas, the Co(II) complexes have an octahedral structure. The proposed structures are given in Figs. 3a and 3b.

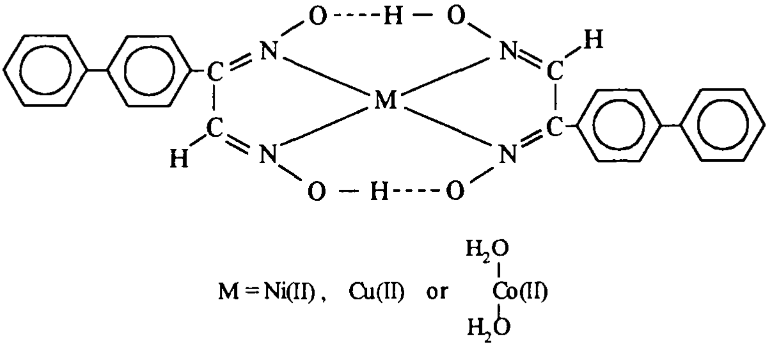

Fig. 3a. Octahedral and Square-planar Structures of the Metal Complexes of Biphenylglyoxime

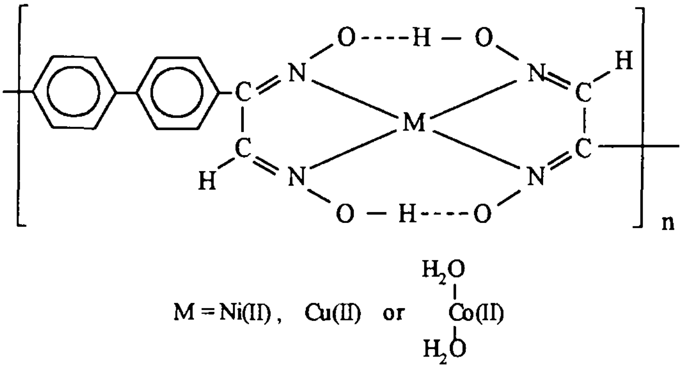

Fig. 3b. Octahedral and Square-planar Structures of the Polymeric Metal Complexes of Bis(phenylglyoxime)

EXPERIMENTAL

Materials and Measurements

The ^{1}H NMR spectra were recorded on a Varian T 100-A spectrometer with deuterated dimethylsulphoxide as solvent, while a Pye Unicam SP 1025 spectrophotometer was used for the IR spectra of the compounds pressed into KBr pellets. The elemental analyses were performed by the Laboratories of the Scientific and Technical Research Council of Turkey (TUBITAK). The physical properties and spectral characteristics of the synthesized compounds are given Tables I, II and III.

Synthesis of 4-Acetylbiphenyl and 4,4'-Diacetylbiphenyl

4-Acetylbiphenyl (4'-phenylacetophenone) and 4,4'-diacetylbiphenyl (biacetophenone) were prepared according to published procedures[13-15] from acetyl chloride and biphenyl in the presence of $AlCl_3$ as catalyst in a Friedel Crafts reaction.

4-Isonitrosoacetylbiphenyl (Keto Oxime) (HL)

A quantity of 0.04 g-atoms (0.92 g) of pure sodium was dissolved in 50 mL absolute ethanol with cooling, and then 0.022 mol (2.26 g) butyl nitrite was added dropwise to the mixture with stirring at about -5 °C. Subsequently, a solution of 0.02 mol (3.92 g) 4-acetylbiphenyl in 50 mL ethanol-benzene (2:1) mixture was added to the previous mixture with stirring. The mixture was then left overnight at room temperature for the precipitate to form. The precipitated substance was filtered, followed by washing with ether, dissolved in the minimum amount of water and reprecipitated by addition of dilute HCl. The precipitate was filtered and recrystallized in ethanol-water (1:1). The crystallized product was filtered, washed with water and dried in a vacuum oven at 50 °C. Yield 3.15 g (70 %).

4-Biphenylglyoxime (H_2L')

A quantity of 0.01 mol (2.25 g) 4-isonitrosoacetylbiphenyl was dissolved in 50 mL ethanol. Subsequently, solutions of 0.011 mol (0.77 g) $NH_2OH.HCl$ and 0.032 mol (2.62 g) CH_3COONa (dissolved in the minimum amount of water) were added with stirring. The reaction mixture was refluxed for 4 h and then excess ethanol in the reaction mixture was removed in vacuo. The precipitate was filtered and then recrystallized in ethanol-water (1:2) mixture. Yield 2.28 g (95 %).

4,4'-Diisonitrosoacetylbiphenyl [Bis(keto oxime)] (H_2L)

A quantity of 0.025 g-atoms (0.058 g) of pure sodium was dissolved in 50 mL absolute ethanol with cooling, and then 0.025 mol (2.57 g) butyl nitrite was added dropwise to the mixture with stirring at about -5 °C. Subsequently, a solution of 0.01 mol (2.38 g) 4,4'-diacetylbiphenyl in 50 mL ethanol-benzene (2:1) was added to the reaction mixture. The continuation of the reaction was similar as described for the preparation of 4-isonitrosoacetylbiphenyl. Yield 1.69 g (57 %).

Bis(phenylglyoxime) (H_4L'')

A quantity of $4x10^{-3}$ mol (1.3 g) bis(keto oxime) was dissolved in 50 mL chloroform-ethanol (1:1) mixture. Subsequently, solutions of $8x10^{-3}$ mol (0.62 g) $NH_2OH.HCl$ and $2.5x10^{-3}$ mol (2.05 g) CH_3COONa were added to the previous mixture by stirring. The reaction mixture was refluxed for 12 h and chloroform was removed in vacuo. The precipitated material was filtered and then recrystallized in ethanol-water (1:2) mixture. Yield 1.15 g (80 %).

The colors, yields, melting points, elemental analyses, ^1H NMR and IR data of these ligands are given in Tables I, II and III.

The Synthesis of the Complexes of the Dioximes

A quantity of $2x10^{-3}$ mol (0.48 g) biphenylglyoxime or $1x10^{-3}$ mol (0.33 g) bis(phenylglyoxime) was dissolved in 30 mL hot ethanol, then the solution of $1x10^{-3}$ mol (0.17 g) of $CuCl_2.2H_2O$, (0.24 g) $NiCl_2.6H_2O$, or (0.24 g) $CoCl_2.6H_2O$ in 20 mL water-ethanol (2:1) mixture was added dropwise with stirring. The pH of the reaction mixture was around 3.0-3.5 and then was adjusted to 5.0-5.5 by adding 1 % NaOH solution. The precipitated complex was kept on a water bath at 60 °C for 30 min, then filtered while hot, washed with water, ethanol and diethyl ether, and dried in vacuo.

The complexes of biphenylglyoxime are slightly soluble in DMSO while the polymeric complexes of bis(phenylglyoxime) are insoluble in organic solvents.

The colors, yields, melting points, elemental analytical results and FT-IR data of the complexes are given in Tables I and III.

REFERENCES

1. L. Tschugaev, *Chem. Ber.*, **40**, 3498 (1907).
2. A. Chakravorty, *Coord. Chem. Rev.*, **13**, 1 (1974).
3. J. V. Burakevich, A. M. Lore and G. P. Volpp, *J. Org. Chem.*, **36**, 1 (1971).
4. H. İ. Uçan and R. Mirzaoğlu, *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 437 (1990).
5. İ. Karataş, G. İrez, M. Sezgin, H. İ. Uçan and A. D. Bedük, *Synth. React. Inorg. Met.-Org. Chem.*, **21**, 1031 (1991).
6. M. A. Deveci, G. İrez, B. Mercimek, A. D. Bedük and N. Sarıkavaklı, *Synth. React. Inorg. Met.-Org. Chem.*, **25**, 1699 (1995).
7. G. N. Schrauzer und J. Kohnle, *Chem. Ber.*, **97**, 3056 (1964).
8. D. D. Carlos and D. A. Shimp, U.S. Patent 3,703,497 (1972); Chem. Abstr., **78**, 30843e (1973).
9. C. G. Wermuth and J. Schwartz, Can. Patent 1,054,149 (1979); Chem. Abstr., **92**, 22256q (1980).
10. G. Leclerc, A. Mann, C. G. Wermuth, N. Bieth and J. Schwartz, *J. Med. Chem.*, **20**, 1657 (1977).
11. B. Rouot, G. Leclerc, C. G. Wermuth, F. Miesch and J. Schwartz, *J. Med. Chem.*, **19**, 1049 (1976).
12. M. E. B. Jones, D. A. Thorton and R. F. Webb, *Macromol. Chem.*, **49**, 62 (1961).
13. L. M. Long and H. R. Henze, *J. Am. Chem. Soc.*, **63**, 1939 (1941).
14. G. J. Sloan and W. R. Vaughan, *J. Org. Chem.*, **22**, 750 (1957).
15. H. E. Ungnade, B. Fritz and L. W. Kissinger, *Tetrahedron*, **19**, Suppl. 1, 235 (1963).
16. H. E. Ungnade, L. W. Kissinger, A. Narath and D. C. Barham, *J. Org. Chem.*, **28**, 134, (1963).
17. G. İrez and Ö. Bekaroğlu, *Synth. React. Inorg. Met.-Org. Chem.*, **13**, 781 (1983).
18. A. Nakamura, A. Konishi and S. Otsuka, *J. Chem. Soc. Dalton Trans.*, 488 (1979).

Received: 24 October 1996 Referee I: K. Moedritzer
Accepted: 15 October 1997 Referee II: K. H. Dahmen