Synthesis and Characterization of New vic-Dioximes and Their Metal Complexes with Cu(II), Ni(II), and Co(II) Salts¹

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Abstract—4-Acetyldiphenyl sulfide and 4,4'-diacetyldiphenyl sulfide were synthesized from diphenyl sulfide and acetyl chloride in the presence of AlCl₃ as catalyst in the Friedel–Crafts reaction. Subsequently, the ketooxime and glyoxime derivatives were also prepared. The metal complexes of the glyoximes, such as copper, nickel, and cobalt complexes were prepared. The BF²⁺ capped Ni(II) mononuclear complex of 4-thiophenoxvphenylglyoxime was prepared. The structures of these ligands were identified by FT-IR, ¹H NMR, and ¹³C NMR spectral data and elemental analysis. The structures of the complexes were identified by FT-IR, elemental analysis, and magnetic measurements.

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INTRODUCTION

Numerous vicinal dioximes (vic-dioxime) and their transition metal complexes have been investigated [1]. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure which is stabilized by hydrogen bonding [2]. The high stability of the complexes with vic-dioxime ligands has been used extensively for various purposes. Oximes are used as additive materials for the improvement of pigments, mechanic oils, epoxy resins and rubber, in industry, etc. [3]. Recently, some oximes and their alkyl, oxyalkyl, and amino derivatives were proved to have physiological and biological activity [4-6]. vic-Dioximes also have received considerable attention as model compounds which mimic biofunctions, such as reduction of vitamin B_{12} [7, 8]. The presence of moderately acidic hydroxy groups and slightly basic nitrogen atoms makes vic-dioxime amphoteric ligands that form square-planar, square-pyramidal, or octahedral complexes with transition metal ions, such as Cu(II), Ni(II) and Co(II), as central atoms [7, 9–11].

The dioxygen binding ability of the bis(dioximate)cobalt(II) complexes has been the focus of considerable attention in recent years and has been extensively involved in the design, synthesis, and characterization of several classes of compounds that have been shown to reversibly bind dioxygen [12]. In addition, a group of macrocylic (E, E)-dioximatocobalt complexes in which the original bridging protons of the bis(dioxime) system were replaced by the BF₂ group, has been widely investigated [13]. This substitution has also enhanced markedly the stability of the dioxygen adduct by removing the labile acidic protons from the vicinal dioxime ligands [14].

In the present paper, we describe the synthesis and characterization of two new ketooximes-4-isonitrosoacetyldiphenyl sulfide (HL) and 4,4'-diisonitrosoacetyldiphenyl sulphide (H₂L), two new glyoximes-4thiophenoxyphenylglyoxime (H_2L') and 4,4'-thiobis(phenylglyoxime)dioxime (H_4L''), transition metal complexes of H_2L' and H_4L'' , and the BF_2^+ capped Ni(II) mononuclear complex of H₂L'.

EXPERIMENTAL

4-Acetyldiphenyl sulfide and 4,4'-diacetyldiphenyl sulfide were prepared according to published methods [15]. All starting materials were commercially available and were of reagent grade. The ¹H NMR and ¹³C NMR spectra and elemental analyses for carbon, hydrogen, and nitrogen were carried out at the laboratories of the Scientific and Technical Research Council of Turkey (TÜBİ TAK). Infrared spectra were recorded on a Perkin Elmer model 1605 FT-IR spectrophotometer as KBr pellets. Metal contents in the compounds were determined on a Varian, Vista AX CCD spectrophotometer. Magnetic moments of the complexes were measured using a Sherwood Scientific model MX1 Gouy magnetic susceptibility balance at room temperature. The pH values were measured on a WTW pH, 537 pH meter.

¹ The text was submitted by the authors in English.

Synthesis of 4-isonitrosoacetyldiphenyl sulfide (ketooxime) (HL). Pure sodium (0.92 g) was dissolved in 50 ml of absolute ethanol with cooling, and then butyl nitrite (2.34 g, 20 mmol) was added drop by drop to the mixture with stirring at about -5° C. Subsequently, a solution of 4-acetyldiphenyl sulfide (4.56 g, 20 mmol) in 35 ml of ethanol-water (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 the addition of dilute HCl. The precipitate was filtered and recrystallized in ethanolwater (1:1). The crystallized product was filtered, washed with water, and dried in a vacuum oven at 50°C. Yield 2.72 g (53 %), mp 108°C.

IR (v, cm⁻¹): 3240 v(O–H), 3026 v(C–H_{ar}), 2877 v(C–H_{aliph}), 2372 v(O–H···O)_{chelate}, 1631 v(C=N), 1018 v(N–O).

¹H NMR (δ , ppm): 9.31 (s., 1H, OH), 7.25–6.98 (d.d., J = 11.0 Hz, 4H, C–H_{ar}), 7.29–7.15 d.t.t. (J = 8.78 Hz, 5H, C–H_{ar}), 8.18 (s., 1 H, C–H_{aliph}).

¹³C NMR (δ , ppm): 124.0 (C¹), 126.7 (C²), 119.6 (C³), 147.5 (C⁴), 147.7 (C⁵), 120.5 (C⁶), 127.6 (C⁷), 135.9 (C⁸), 164.3 (C⁹), 157.1 (C¹⁰).

Synthesis of 4-thiophenoxyphenylglyoxime (dioxime) (H₂L'). 4-Isonitrosoacetyldiphenyl sulfide (2.57 g, 10 mmol) was dissolved in 50 ml of ethanol. Subsequently, solutions of NH₂OH \cdot HCl (0.77 g, 11 mmol) and CH₃COONa (2.62 g, 32 mmol) (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 an ethanol–water (1 : 2) mixture. Yield 1.87 g (69 %), mp 169°C.

IR (v, cm⁻¹): 3247 v(O–H), 3023 v(C–H_{ar}), 2908 v(C–H_{aliph}), 2376 v(O–H…N)_{chelate}, 1692 v(C=N), 978 v_e(N–O).

¹H NMR (δ , ppm): 9.07 (s., 1H, OH^a), 8.62 (s., 1H, OH^b), 7.22–7.01 (d.d., J = 10.7 Hz, 4H, C–H_{ar}), 7.28–7.11 (d.t.t., J = 8.59 Hz, 5H, C–H_{ar}), 8.13 (s., 1 H, C–H_{aliph}).

¹³C NMR (δ , ppm): 123.7 (C¹), 126.5 (C²), 119.4 (C³), 147.2 (C₄), 147.6 (C⁵), 119.3 (C⁶), 122.7 (C⁷), 135.8 (C⁸), 156.7 (C⁹), 156.8 (C¹⁰).

Synthesis of 4,4'-diisonitrosoacetyldiphenyl sulfide [bisketooxime)] (H₂L). Pure sodium (0.58 g) was dissolved in 50 ml of absolute ethanol with cooling, and then butyl nitrite (2.93 g, 25 mmol) was added drop by drop to the mixture with stirring at about -5° C. Subsequently, a solution of 4,4'-diacetyldiphenyl sulfide (2.70 g, 10 mmol) in 50 ml of ethanol–water (2 : 1) was added to the reaction mixture. The continuation of the reaction was similar as described for the preparation of 4-isonitrosoacetyldiphenyl sulfide. Yield 1.60 g (49 %), mp 163°C.

IR (v, cm⁻¹): 3249 v(O–H), 3028 v(C–H_{ar}), 2878 v(C–H_{aliph}), 2380 v(O–H···O)_{chelate}, 1619 v(C = N), 1007 v(N–O).

¹H NMR (δ , ppm): 9.28 (s., 2H, OH), 7.30–7.14 (d.d., J = 8.20 Hz, 4H, C–H_{ar}), 8.11 (s., 2 H, C–H_{aliph}).

¹³C NMR (δ, ppm): 147.2 (C¹), 126.2 (C²), 127.3 (C³), 135.7 (C⁴), 164.2 (C⁵), 157.0 (C⁶).

Synthesis of 4,4'-thio-bis(phenylglyoxime) (dioxime) (H₄L''). Bis(ketooxime) (1.31 g, 4.0 mmol) was dissolved in 50 ml of a chloroform–ethanol (1 : 1) mixture. Subsequently, solutions of NH₂OH · HCl (0.55 g, 8 mmol) and CH₃COONa (2.05 g, 2.5 mmol) were added to the previous mixture with stirring. The reaction mixture was refluxed for 12 h, and chloroform was removed in vacuo. The precipitated material was filtered and then recrystallized in anethanol–water (1 : 2) mixture. Yield 0.96 g (67%), mp 219°C.

IR (v, cm⁻¹): 3277 v(O–H), 3017 v(C–H_{ar}), 2874 v(C–H_{aliph}), 2372 v(O–H···N)_{chelate}, 1693 v(C=N), 988 v(N–O).

¹H NMR (δ , ppm): 9.02 (s., 2H, OH^a), 8.27 (s., 2H, OH^b), 7.18–6.96 (d.d., J = 8.40 Hz, 4H, C–H_{ar}), 8.20 (s., 2H, C–H_{aliph}).

¹³C NMR (δ, ppm): 147.0 (C¹), 125.9 (C²), 126.9 (C³), 135.4 (C⁴), 155.7 (C⁵), 156.8 (C⁶).

Synthesis of the Cu(II), Ni(II) and Co(II) complexes of the dioximes. 4-Thiophenoxyphenylglyoxime (0.54 g, 2.0 mmol) or 4,4'-thio-bis(phenylglyoxime) (0.36 g, 1.0 mmol) was dissolved in 30 ml of hot ethanol. Then a solution of (1.00 mmol) Cu(NO₃)₂ · $2H_2O$, NiCl₂ · $6H_2O$ or Co(NO₃)₂ · $6H_2O$ (2 : 1) in 20 ml of a water–ethanol mixture was added drop by drop with stirring. The pH of the reaction mixture was around 3.5–4.0 and was then adjusted to 5.5–6.0 by adding a 1% NaOH solution. The precipitated complex was kept in a water bath at 60°C for 1 h in order to complete the precipitation. The precipitate was filtered off, washed with water, ethanol, and diethyl ether, and dried.

Synthesis of $[(L'BF_2)_2Ni]$. A suspension of $(HL')_2Ni$ (0.3 g, 0.5 mmol) in 50 ml of freshly distilled dry acetonitrile was brought to the reflux temperature in a nitrogen atmosphere. An equivalent amount of boron-trifluoride etherate complex (0.41 ml) was added with continuous stirring to this suspension, which changed its color to red immediately. After refluxing for 30 min, the solvent was evaporated to dryness. Then the dark red crude product was dissolved in 10 ml of dry acetonitrile and

allowed to stand in a refrigerator at -18° C overnight, whereupon the compound crystallized from the solution. The red crystallized product was collected by filtration, washed with cold acetonitrile and diethyl ether, and then dried in vacuo.

The colors, yields, melting points, elemental analysis, and FT-IR data, magnetic moments of these compounds are given in Tables 1 and 2, respectively.

RESULTS AND DISCUSSION

4-Acetyldiphenyl sulfide and 4,4'-diacetyldiphenyl sulfide were obtained by the reaction of acetyl chloride with diphenyl sulfide in the presence of AlCl₃ as catalyst in the Friedel–Crafts reaction [15]. Ketooximes (HL and H₂L) and dioximes (H₂L' and H₄L") of these compounds were originally synthesized by a described procedure [16]. The structures of keto-oximes and dioximes (ligands) are given bellow:



In the ¹H NMR spectra of the oximes, two peaks are present for the OH protons of the dioxime groups (H₂L' and H₄L"), while the OH protons of the ketooximes (HL and H₂L) appear as singlet peaks. When the chemical shift values of the two OH groups in the dioximes are compared, those in the lower field quite closely resemble each other (9.07–9.02 ppm), while a considerable difference is observed for those in the higher field (8.62–8.27 ppm) [17, 18]. The chemical shifts of the C–H protons adjacent to the oxime groups and the aromatic protons are in a range of 8.20–8.11 and 7.30–6.96 ppm, respectively. All these values are in agreement with the chemical shift values of oxime protons [19, 20].

In the ¹³C NMR spectrum of the ligands (H_2L' and H_4L''), the signals at 156.8–156.7 and 156.8–155.7 ppm are attributed to the carbon atoms of the oxime groups, respectively. In the ¹³C NMR spectrum of the ligands (HL and H_2L), the signals at 164.3–164.2 and 157.1–157.0 ppm are attributed to the carbonyl carbon atom and the carbon atom of the oxime group, respectively.

All the signals in the 147.7–119.4 ppm range are assigned to the carbon atoms of the aromatic rings. All these values are in agreement with those reported previously [20].

The FT-IR data for characterizing the structures of the complexes are given in Table 2. In the FT-IR spectra of the oximes, O–H stretching vibrations appear as a broad absorption at 3277–3240 cm⁻¹. Bands due to C=N and N–O stretches appear at 1693–1619 and 1018–978 cm⁻¹, respectively. These absorption data are in agreement with those previously reported for other oxime derivatives [21, 22]. Bands appearing at 2380–2372 cm⁻¹ in the ketooximes and dioximes indicate that there are intermolecular H-bridges.



The Cu(II), Ni(II), and Co(II) complexes of the oximes were obtained in an ethanol-water (1:1) mixture by the addition of sufficient 1% NaOH to increase the pH to 5.0-5.5. Some physical properties of the complexes are given in Tables 1 and 2. The structures of the complexes were characterized by FT-IR, elemental analysis, and magnetic measurements. ¹H NMR spectra of the complexes could not be taken because of their very low solubility in organic solvents. In the FT-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 the metal and nitrogen atoms of the dioximes. The weak bands appearing around 1737-1719 cm⁻¹ in the FT-IR spectra of the complexes correspond to intermolecular hydrogen bridges (O-H...O), but these peaks are missing in the spectra of the ligands. In addition, the broad peaks appearing around 3418–3391 cm⁻¹ in the spectra of the Co(II) complexes indicate that H₂O is coordinated to Co(II).

The $[(L'BF_2)_2Ni]$ complex was prepared from boron trifluoride and complex $[(HL')_2Ni]$ in acetonitrile. In the FT-IR spectrum of $[(L'BF_2)_2Ni]$, the broad band at 1722 cm⁻¹ due to O–H···O bending vibrations disappeared upon encapsulation of the hydrogen-bridged complex with BF₂ with the concomitant appearance of peaks at 1162 and 832 cm⁻¹ for the B–O and B–F vibrations, respectively [23]. This complex exhibits upward shifts in the stretching vibrations of the azomethine groups, owing to the BF_2 groups [24].

When the elemental analyses of the complexes were carried out, the metal-ligand ratios were found to be 1:2 in the complexes of 4-thiophenoxyphenylglyoxime and 1:1 in the polymeric complexes of 4,4'-thiobis(phenylglyoxime). The molecular weights of polymeric metal complexes of 4,4'-thio-bis(phenylglyoxime) could not be determined because of their insolubility in organic solvents. The Ni(II) and Cu(II) complexes with the ligands H_2L' and H_4L'' are diamagnetic. The room temperature magnetic moments of the Co(II) complexes with the ligands H₂L' and H₄L" are paramagnetic with magnetic susceptibility values of 3.93 and 3.98 $\mu_{\rm B}$, respectively. The effective magnetic moments of the octahedral Co(II) complexes were 4.10 and $4.30 \,\mu_B$, respectively [25]. The magnetic data of the Co(II) complexes agree with a d^7 metal ion in a squareplanar field or an octahedral configuration [26, 27].

According to the FT-IR data, elemental analysis, and magnetic measurements, the Ni(II) and Cu(II) complexes have a square-planar structure, whereas the Co(II) complexes have an octahedral structure. Magnetic susceptibility measurements of the complexes provide information regarding their structures and are shown in Table 2. The structures of the obtained complexes are given bellow:



bis(phenylglyoxime); M = Ni(II), Cu(II), and Co(II). OH₂

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 33 No. 3 2007



Square-planar structure of the BF₂⁺-capped Ni(II) mononuclear complex of 4-thiophenoxyphenylgyoxime.

Table 1. The elemental analysis data and some physical properties of ketooximes, glyoximes, and its complexes

Compound	Empirical formula	Color	M.p., °C	Yield, g (%)	Content (found/calcd), %			
					С	Н	N	metals
HL	C ₁₄ H ₁₁ NO ₂ S	White	108	2.72 (53)	65.29/65.36	4.23/4.28	5.39/5.44	
H ₂ L'	$C_{14}H_{12}N_2O_2S$	Cream	169	1.87 (69)	61.68/61.76	4.33/4.41	10.22/10.29	
H ₂ L	$C_{16}H_{12}N_2O_4S$	Cream	163	1.60 (49)	58.47/58.53	3.59/3.65	8.45/8.53	
H ₄ L"	$C_{16}H_{14}N_4O_4S$	Yellow	219	0.96 (67)	53.54/53.63	3.83/3.91	15.55/15.64	
$[(HL')_2Cu]$	$C_{28}H_{22}N_4O_4S_2Cu$	Green	>300	1.03 (85)	55.39/55.48	3.57/3.63	9.15/9.24	10.44/10.49
[(HL')2Ni]	$\mathrm{C}_{28}\mathrm{H}_{22}\mathrm{N}_4\mathrm{O}_4\mathrm{S}_2\mathrm{Ni}$	Red	>300	1.04 (87)	55.86/55.93	3.57/3.66	9.21/9.32	9.68/9.77
[(L'BF ₂) ₂ Ni]	$C_{28}H_{20}N_4O_4S_2B_2F_4Ni$	Red	285*	0.98 (75)	48.18/48.11	3.09/3.15	7.93/8.02	8.32/8.40
$[(\mathrm{HL'})_2\mathrm{Co}(\mathrm{H}_2\mathrm{O})_2]$	$C_{28}H_{26}N_4O_6S_2Co$	Brown	>300	1.09 (86)	52.64/52.75	3.99/4.08	8.68/8.79	9.18/9.25
$[(H_2L'')Cu]_n$	$[\mathbf{C}_{16}\mathbf{H}_{12}\mathbf{N}_4\mathbf{O}_4\mathbf{S}\mathbf{C}\mathbf{u}]_n$	Green	>300	0.35 (83)	45.69/45.76	2.77/2.86	13.23/13.34	15.08/15.14
$[(H_2L'')Ni]_n$	$[\mathrm{C}_{16}\mathrm{H}_{12}\mathrm{N}_4\mathrm{O}_4\mathrm{SNi}]_n$	Red	>300	0.35 (85)	45.88/45.96	2.79/2.87	13.32/13.40	13.98/14.05
$[(\mathrm{H}_{2}\mathrm{L}'')\mathrm{Co}(\mathrm{H}_{2}\mathrm{O})_{2}]_{n}$	$[C_{16}H_{16}N_4O_6SCo]_n$	Brown	>300	0.38 (84)	42.48/42.57	3.50/3.54	12.33/12.42	19.97/13.07

* Decomposition point.

Table 2. Data of magnetic measurements and characteristic IR spectra of the complexes

Compound	Empirical formula	μ_{eff}, μ_B	$\nu(\mathrm{H_2O})$	v(C-H) _{Ar}	$\nu(CH)_{Aliph}$	v(C=N)	v(N-O)	ν(O…H–O)
[(HL') ₂ Cu]	$C_{28}H_{22}N_4O_4S_2Cu$	Dia		3009 w*	2800 m*	1654 s*	989 s*	1720 s
[(HL') ₂ Ni]	$C_{28}H_{22}N_4O_4S_2N_1$	Dia		3018 w	2885 m	1656 s	1003 s	1722 s
[(L'BF ₂) ₂ Ni]	$C_{28}H_{20}N_4O_4S_2B_2F_4Ni$	Dia		3015 w	2880 m	1675 s	985 s	
$[(HL')_2Co(H_2O)_2]$	$C_{28}H_{26}N_4O_6S_2Co$	4.93	3418 s	3044 w	2938 m	1647 s	1008 s	1737 s
$[(H_2L'')Cu]_n$	$[C_{16}H_{12}N_4O_4SCu]_n$	Dia		3024 w	2918 m	1648 s	1004 s	1723 s
$[(H_2L'')Ni]_n$	$[C_{16}H_{12}N_4O_4SNi]_n$	Dia		3029 w	2927 m	1664 s	994 s	1719 s
$[(\mathrm{H}_{2}\mathrm{L}'')\mathrm{Co}(\mathrm{H}_{2}\mathrm{O})_{2}]_{n}$	$[C_{16}H_{16}N_4O_6SCo]_n$	4.98	3391 s	3048 w	2937 m	1653 s	1010 s	1727 s

* s-strong, m-medium, w-weak.

The above values of FT-IR, ¹H NMR, ¹³C NMR, elemental analysis, data and magnetic susceptibility are in agreement with those previously reported, particularly those of bis(phenylglyoxime) [28] and other glyoximes [17, 21, 25].

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