

The Synthesis of 4-Phenoxyphenylglyoxime and 4,4'-Oxybis(phenylglyoxime) and Their Complexes with Cu(II), Ni(II) and Co(II)

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4-Acetyldiphenyl ether and 4,4'-diacetyldiphenyl ether were synthesized from diphenyl ether and acetyl chloride in the presence of AlCl₃ used as catalyst. Subsequently, their keto oxime and glyoxime derivatives were prepared. The metal complexes of the glyoximes such as Cu(II), Ni(II) and Co(II) were also prepared. The structures of these ligands and their complexes were identified by FT-IR, ¹H NMR and ¹³C NMR spectral data, elemental analysis and magnetic measurements.

Key Words: Keto oxime, Glyoxime, Transition metal complexes.

Introduction

Vic-dioximes and their derivatives are a very important class of ligands, forming complexes with transition metal cations. Complexes of these compounds were firstly prepared by Tschugaev in 1907 and their numbers have increased since then¹⁻⁷. Some oximes are widely used for various purposes in organic, analytical, inorganic, bio and industrial chemistry⁸. For example, *vic*-dioximes have received considerable attention as model compounds that mimic biofunctions, such as the reduction of vitamin B₁₂^{2,8}. Oximes are used as additive materials for the improvement of pigments, mechanic oils, epoxy resins and rubber, in industry, etc.⁹. Recently, some oximes and their alkyl, oxyalkyl and amino derivatives were proved to have physiological and biological activity¹⁰⁻¹².

The presence of mildly 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^{2,8,13}.

The synthesis and characterization of 2 new keto oximes and 2 new glyoximes and transition metal cation complexes of 4-phenoxyphenylglyoxime and 4,4'-oxybis(phenylglyoxime) are explored in this study.

Materials and Measurements

All starting materials were commercially available and were of reagent grade. The ^1H NMR, ^{13}C NMR spectra and elemental analysis for carbon, hydrogen and nitrogen were carried out by the laboratories of the Scientific and Technological Research Council of Turkey (TÜBİTAK). Infrared spectra were recorded on a Perkin Elmer model 1605 FT-IR spectrophotometer as KBr pellets. Metal contents of the compounds were determined on a Varian, Vista AX CCD simultaneous spectrophotometer. The 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 537 pH meter.

Experimental

Synthesis of 4-acetyldiphenyl ether

4-Acetyldiphenyl ether (4'-phenoxyacetophenone) was prepared according to the methods described in the literature¹⁴, yield, 4.9 g (76%), mp. 40 °C [Lit¹⁴: 40-41 °C].

Synthesis of 4,4'-diacetyldiphenyl ether

4,4'-Diacetyldiphenyl ether [(oxybis(acetophenone))] was prepared according to the methods described in the literature¹⁵, yield, 5.9 g (78%), mp. 101 °C [Lit¹⁵: 100-101 °C].

Synthesis of 4-isonitrosoacetyldiphenyl ether (Keto oxime) (HL)

A quantity of 0.04 g-atoms (0.92 g) of pure sodium was dissolved in 50 mL of absolute ethanol with cooling, and then (2.34 g, 20 mmol) butyl nitrite was added dropwise to the mixture with stirring at about -5 °C. Subsequently, a solution of (4.2 g, 20 mmol) 4-acetyldiphenyl ether in 35 mL of ethanol-benzene (2:1) mixture was added to the previous mixture with stirring. The mixture was then left overnight at room temperature for complete precipitation. 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 ethanol-water (1:1). The crystallized product was filtered, washed with water and dried in a vacuum oven at 50 °C, yield, 2.5 g (52%), mp. 102 °C.

Synthesis of 4-phenoxyphenylglyoxime ($\text{H}_2\text{L}'$)

A quantity of (2.41 g, 10 mmol) 4-Isonitrosoacetyldiphenyl ether was dissolved in 50 mL of ethanol. Subsequently, solutions of (0.77 g, 11 mmol) $\text{NH}_2\text{OH}\cdot\text{HCl}$ and (2.62 g, 32 mmol) 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 an ethanol-water (1:2) mixture, yield, 1.75 g (68%), mp. 161 °C.

Synthesis of 4,4'-diisonitrosoacetyldiphenyl ether [bis(keto oxime)] (H_2L)

4,4'-Diisonitrosoacetyldiphenyl ether was prepared following the same procedure as described for 4-isonitrosoacetyldiphenyl ether, starting from 0.025 g-atoms (0.58 g) of pure sodium, (2.93 g, 25 mmol) butyl nitrite

and (2.54 g, 10 mmol) 4,4'-diacetyldiphenyl ether, yield, 1.56 g (50%), mp. 155 °C.

Synthesis of 4,4'-oxybis(phenylglyoxime) (H₄L'')

4,4'-Oxybis(phenylglyoxime) was prepared following the same procedure as described for 4-phenoxyphenylglyoxime, starting from (1.25 g, 4.0 mmol) bis(keto oxime), (0.55 g, 8 mmol) NH₂OH.HCl and (2.05 g, 2.5 mmol) CH₃COONa, yield, 0.95 g (69%), mp. 207 °C.

The colors, elemental analysis, ¹H NMR, ¹³C NMR and FT-IR data of these ligands are given in Tables 1-4.

Synthesis of the Cu(II), Ni(II) and Co(II) complexes of the dioximes

A quantity of (0.50 g, 2.0 mmol) 4-phenoxyphenylglyoxime or (0.34 g, 1.0 mmol) 4,4'-oxybis(phenylglyoxime) was dissolved in 30 mL of hot ethanol. Then the solution of 1.00 mmol Cu(NO₃)₂.2H₂O, NiCl₂.6H₂O or Co(NO₃)₂.6H₂O in 20 mL of water-ethanol (2:1) mixture was added dropwise 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 1% NaOH solution. The complex product 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 then dried. The colors, yields, melting points, elemental analysis and FT-IR data of the complexes are given in Tables 1 and 4.

Table 1. Some physical properties and elemental analysis of the ligands and complexes.

Compounds	Color	M.p. (°C)	Yield (%)	Calculated (Found) % of			
				C	H	N	Metals
[C ₁₄ H ₁₁ NO ₃]	White			69.7	4.56	5.8	-
HL				(69.48)	(4.51)	(5.69)	
[C ₁₄ H ₁₂ N ₂ O ₃]	Cream			65.62	4.68	10.93	-
H ₂ L'				(65.51)	(4.63)	(10.84)	
[C ₁₆ H ₁₂ N ₂ O ₅]	Cream			61.54	3.84	8.97	-
H ₂ L				(61.47)	(3.78)	(8.88)	
[C ₁₆ H ₁₄ N ₄ O ₅]	Yellow			56.14	4.09	16.37	-
H ₄ L''				(56.09)	(4.02)	(16.29)	
[(C ₁₄ H ₁₁ N ₂ O ₃) ₂ Cu]	Green	>300	86	58.58	3.83	9.76	11.07
[(HL') ₂ Cu]				(58.5)	(3.77)	(9.69)	(11.03)
[(C ₁₄ H ₁₁ N ₂ O ₃) ₂ Ni]	Red	>300	88	59.08	3.87	9.84	10.32
[(HL') ₂ Ni]				(58.99)	(3.8)	(9.78)	(10.26)
[(C ₁₄ H ₁₁ N ₂ O ₃) ₂ Co.2H ₂ O]	Brown	>300	87	59.05	3.87	9.84	10.35
[(HL') ₂ Co(H ₂ O) ₂]				(58.94)	(3.81)	(9.76)	(10.3)
[C ₁₆ H ₁₂ N ₄ O ₅ Cu] _n	Green	>300	85	47.58	2.97	13.88	15.74
[(H ₄ L'')Cu] _n				(47.49)	(2.9)	(13.79)	(15.66)
[C ₁₆ H ₁₂ N ₄ O ₅ Ni] _n	Red	>300	86	48.15	3	14.04	14.72
[(H ₄ L'')Ni] _n				(48.09)	(2.92)	(13.93)	(14.65)
[C ₁₆ H ₁₂ N ₄ O ₅ Co.(H ₂ O) ₂] _n	Brown	>300	88	44.14	2.76	12.87	14.77
[(H ₄ L'')Co(H ₂ O) ₂] _n				(44.08)	(2.68)	(12.78)	(14.71)

Table 2. ^1H NMR spectral data of the ligands in DMSO- d^6 , (δ , ppm).

Compounds	O-H ^a	O-H ^b	C-H (arom)	C-H(aliph)
[C ₁₄ H ₁₁ NO ₃]	9.35	-	7.29-7.02	8.20
HL	(s, 1H)		(d,d J = 11.1 Hz, 4 H) 7.34 (t, J _{1,2} = 8.68 Hz, 1H, H ₁) 7.18 (dd, J _{2,1} = 8.68 Hz, J _{2,3} = 8.94 Hz, 1H, H ₂)	(s, 1H)
[C ₁₄ H ₁₂ N ₂ O ₃]	9.10	8.65	7,25-7.05	8.15
H ₂ L'	(s, 1H)	(s, 1H)	(d,d J = 10.8 Hz, 4 H) 7.30 (t, J _{1,2} = 8.48 Hz, 1H, H ₁) 7.12 (dd, J _{2,1} = 8.48 Hz, J _{2,3} = 8.72 Hz, 1H, H ₂)	(s, 1H)
[C ₁₆ H ₁₂ N ₂ O ₅]	9.30	-	7.32-7.15	8.12
H ₂ L	(s, 1H)		(d,d J = 8.20 Hz, 4 H)	(s, 2H)
[C ₁₆ H ₁₄ N ₄ O ₅]	9.05	8.30	7.21-6.99	8.23
H ₄ L''	(s, 2H)	(s, 2H)	(d,d J = 8.42 Hz, 4 H)	(s, 2H)

s: singlet, d: duplet, t: triplet

Table 3. ^{13}C NMR spectral data of the ligands (DMSO- d^6).

Compounds	δ (ppm)				
[C ₁₄ H ₁₁ NO ₃]	C(1) 124.4	C(2) 127.3	C(3) 120.4	C(4) 148.5	
HL	C(5) 148.7	C(6) 121.1	C(7) 128.0	C(8) 136.1	
	C(9) 164.4	C(10) 157.2			
[C ₁₄ H ₁₂ N ₂ O ₃]	C(1) 124.1	C(2) 127.1	C(3) 120.2	C(4) 148.2	
H ₂ L'	C(5) 148.6	C(6) 119.9	C(7) 128.1	C(8) 136.0	
	C(9) 156.8	C(10) 156.9			
[C ₁₆ H ₁₂ N ₂ O ₅]	C(1) 148.2	C(2) 126.8	C(3) 127.7	C(4) 135.9	
H ₂ L	C(5) 164.3	C(6) 157.1			
[C ₁₆ H ₁₄ N ₄ O ₅]	C(1) 148.0	C(2) 126.5	C(3) 127.3	C(4) 135.6	
H ₄ L''	C(5) 155.8	C(6) 156.9			

Results and Discussion

4-Acetyldiphenyl ether¹⁴ and 4,4'-diacetyldiphenyl ether¹⁵ were obtained by the reaction of acetyl chloride with diphenyl ether in the presence of AlCl₃ as catalyst in a Friedel-Crafts reaction^{13,14}. Keto oximes (HL and H₂L) and dioximes (H₂L' and H₄L'') of these compounds were originally synthesized by following the literature³. The structures of these compounds were identified by elemental analysis, ^1H NMR, ^{13}C NMR and FT-IR, as shown in Tables 1-4.

Table 4. Magnetic measurements and characteristic IR bands (cm^{-1}) of the oximes and their complexes as KBr pellets.

Compounds	μ_{eff} (B.M.)	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)
$[\text{C}_{14}\text{H}_{11}\text{NO}_3]$	-	3245	3030	2880	2380	1635	1020	-
HL								
$[\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3]$	-	3250	3025	2910	2385	1695	980	-
$\text{H}_2\text{L}'$								
$[\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_5]$	-	3250	3030	2880	2390	1620	1010	-
H_2L								
$[\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_5]$	-	3280	3020	2875	2380	1695	990	-
$\text{H}_4\text{L}''$								
$[(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3)_2\text{Cu}]$	Dia	-	3010	2800	-	1655	990	1720
$(\text{HL}')_2\text{Cu}$								
$[(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3)_2\text{Ni}]$	Dia	-	3020	2890	-	1660	1005	1725
$(\text{HL}')_2\text{Ni}$								
$[(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3)_2\text{Co}]$	3.95	3420	3045	2940	-	1650	1010	1740
$(\text{HL}')_2\text{Co}(\text{H}_2\text{O})_2$								
$[\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_5\text{Cu}]_n$	Dia	-	3025	2920	-	1650	1005	1725
$[(\text{H}_4\text{L}')\text{Cu}]_n$								
$[\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_5\text{Ni}]_n$	Dia	-	3030	2930	-	1665	995	1720
$[(\text{H}_4\text{L}'')\text{Ni}]_n$								
$[\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_5\text{Co}(\text{H}_2\text{O})_2]_n$	3.99	3395	3050	2940	-	1655	1010	1730
$[(\text{H}_4\text{L}'')\text{Co}(\text{H}_2\text{O})_2]_n$								

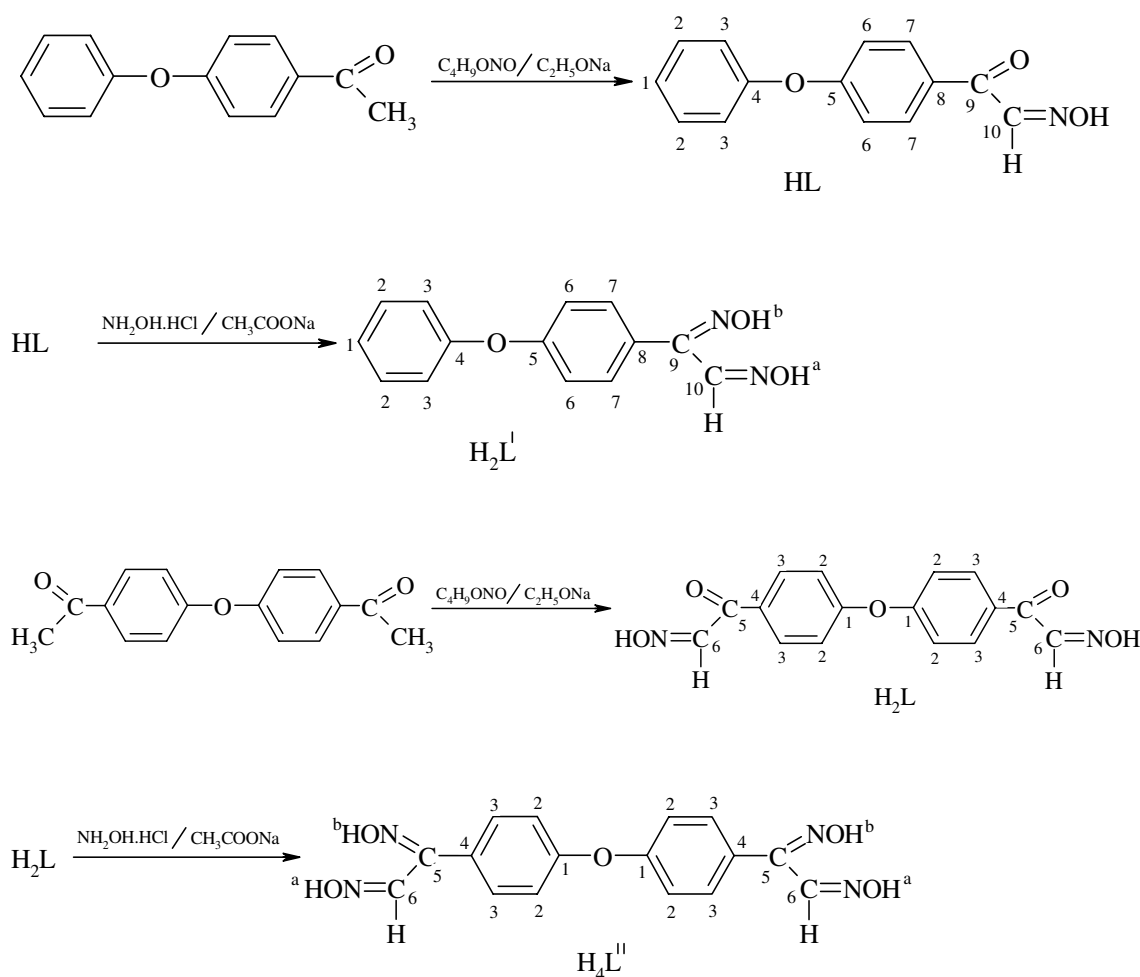


Figure 1. The structures of the keto oximes and dioximes (ligands).

In the 1H NMR spectra of the oximes, 2 peaks are present for the OH protons of the dioxime groups (**H₂L'** and **H₄L''**), while the OH protons of the keto oximes (**HL** and **H₂L**) appear as singlet peaks. When the chemical shift values of the 2 OH groups in the dioximes are compared, the ones at the lower field resemble each other quite closely (9.10-9.05 ppm), while a considerable difference is observed for those at the higher field (8.65-8.30 ppm)^{5,6}. The chemical shifts of the C-H protons adjacent to the oxime groups and the aromatic protons are at 8.23-8.12 ppm and 7.34-6.99 ppm, respectively. All these values are in agreement with the chemical shift values of oximes protons^{16,17}, which are given in Table 2.

In the ^{13}C NMR spectrum of the ligands (**H₂L'** and **H₄L''**), the signals at 155.3-153.8 and 157.7-155.8 ppm are attributed to the carbon atoms of the oxime groups, respectively.

In the ^{13}C NMR spectrum of the ligands (**HL** and **H₂L**), the signals at 164.4-164.3 ppm and 157.2-157.1 ppm are attributed to the carbonyl carbon atom and the carbon atom of the oxime group, respectively. All the signals in the 148.7-118.7 ppm range are assigned to the carbon atoms of the aromatic rings. All these values are in agreement with the previously reported²⁰ ones (Table 3).

FT-IR data for characterizing the structure of the ligands and their complexes are given in Table 4. In the FT-IR spectra of the oximes, O-H stretching vibrations appear as a broad absorption at 3280-3245 cm^{-1} . Bands due to C = N and N-O stretches appear at 1695-1620 and 1020-980 cm^{-1} , respectively. These

absorption data are in agreement with other oxime derivatives reported previously in the literature^{18,19}. Bands appearing at 2390-2380 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 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 complexes are given in Tables 1 and 4. The structures of the complexes were characterized by FT-IR, elemental analysis and magnetic measurements. ¹H NMR spectra of the complexes could not be obtained 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 metal and the nitrogen atoms of the dioximes. The weak bands appearing at around 1740-1720 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 ligands. In addition, the broad peaks appearing at around 3420-3395 cm^{-1} in the Co(II) complexes indicate that H₂O is coordinated to Co(II).

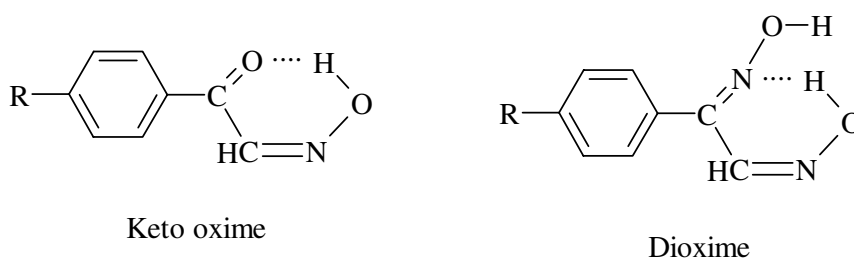


Figure 2. The hydrogen bridges in the keto oximes and dioximes.

When the elemental analysis of the complexes was investigated, the metal-ligand ratios were found to be 1:2 in the complexes of 4-phenoxyphenylglyoxime and 1:1 in the polymeric complexes of 4,4'-oxybis(phenylglyoxime). The molecular weights of polymeric metal complexes of 4,4'-oxybis(phenylglyoxime) could not be determined because of their insolubility in organic solvents. The Ni(II) and Cu(II) complexes of the ligands (H₂L' and H₄L'') are diamagnetic. The room temperature magnetic moments of the Co(II) complexes of the ligands (H₂L' and H₄L'') are paramagnetic, with magnetic susceptibility values of 3.95 and 3.99 B.M., respectively. The effective magnetic moment values of the octahedral Co(II) complexes were 4.10 and 4.30 B.M., respectively²⁰. The magnetic data of the Co(II) complexes agree with a d⁷ metal ion in a square-planar or an octahedral configuration^{21,22}.

According to the FT-IR data, elemental analysis and magnetic measurements results, 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 on their structures as shown in Table 4. The structures of the complexes are shown in Figures 3 and 4.

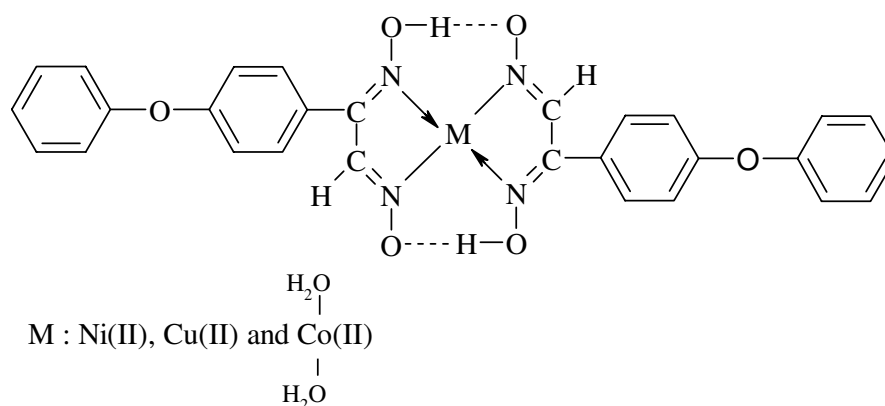


Figure 3. Octahedral and square-planar structures of the metal complexes of 4-phenoxyphenylglyoxime (H_2L').

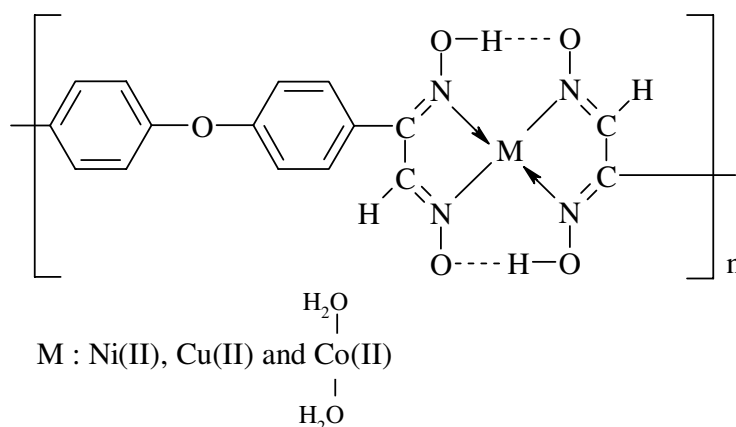


Figure 4. Octahedral and square-planar structures of the metal complexes of 4,4'-oxybis(phenylglyoxime) (H_4L'').

The above values of FT-IR, 1H NMR, ^{13}C NMR, elemental analysis and magnetic susceptibility are in agreement with those previously reported, particularly those of bis(phenylglyoxime)²³⁻²⁶ and other aminoglyoximes^{16,17,19,20}.

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