

The Synthesis of Substituted 4,4'-Thiobis(Aminophenylglyoxime) and Their Polymeric Metal Complexes with Cu(II), Ni(II) and Co(II) Salts

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Received 30.07.2003

4,4'-Bis(chloroacetyl)diphenyl thioether (HL) was synthesized from chloroacetyl chloride and diphenyl thioether in the presence of AlCl₃ as catalyst in a Friedel-Crafts reaction. Subsequently, its keto oxime (H₂L) and glyoxime (H₄L) derivatives were also prepared. Then 3 new substituted 4,4'-thiobis(aminophenylglyoxime) (H₄L¹⁻³) were synthesized from 4,4'-thiobis(chlorophenylglyoxime) and the corresponding amines. The Ni(II), Cu(II) and Co(II) complexes of these ligands were prepared. The structures of these ligands and their complexes were identified by FT-IR, ¹H NMR and ICP-AES spectral data, elemental analyses and magnetic measurements.

Key Words: Glyoxime, Transition metal complexes.

Introduction

Oximes have been widely recognized as ligands since the *vic*-dioxime metal complex bis-methylglyoximate-nickel(II) was discovered by Tschugaeff¹. *Vic*-dioximes and their derivatives are a very important class of ligands, forming complexes with transition metals. The coordination chemistry of *vic*-dioximes is interesting and numerous transition metal complexes of these ligands have been investigated¹⁻⁶. Some oximes are widely used for various purposes in organic, analytical, inorganic, bio and industrial chemistry. For example, *vic*-dioximes have received considerable attention as model compounds that mimic biofunctions, such as the reduction of vitamin B₁₂^{2,7}. On the other hand, oxime metal chelates are biologically active⁸ and semiconducting⁹⁻¹⁰.

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^{2,7-11}.

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This article describes the synthesis and characterization of 3 new substituted 4,4'-thiobis(aminophenylglyoxime) and their transition metal complexes.

Materials and Measurements

All starting materials were commercially available and were of reagent grade. The ^1H NMR spectra and elemental analyses for carbon, hydrogen and nitrogen were carried out by the laboratories of the Scientific and Technical 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 pH, 537 pH meter.

Experimental

Synthesis of 4,4'-bis(chloroacetyl)diphenyl thioether [HL]

4,4'-Bis(chloroacetyl)diphenyl thioether was prepared according to the methods described in the literature¹². Diphenyl thioether (9.3 g, 49.92 mmol) was dissolved in CS_2 (30 mL) and the solution was added dropwise to a suspension of anhydrous AlCl_3 (20 g, 150 mmol) and chloroacetyl chloride (12 mL, 150.5 mmol) in CS_2 (20 mL) with cooling. The mixture was stirred at an ambient temperature until the evolution of HCl ceased (about 12 h). After removal of the solvent by rotary evaporator, the residue was recrystallized from EtOH. Yield: 8.3 g (49%), m.p.: 106 °C [Lit¹²: 106-107 °C].

Synthesis of 4,4'-thiobis(phenylglyoxylohydroximoyl chloride) [H₂L]

4,4'-Thiobis(phenylglyoxylohydroximoyl chloride) was prepared using the method described in the literature¹³. 4,4'-Bis(chloroacetyl)diphenyl thioether (3.39 g, 10 mmol) was dissolved in CHCl_3 (70 mL) with cooling, and then HCl gas was bubbled through the solution for 30 min. Butyl nitrite (3 mL, 22 mmol) was added dropwise to the mixture with stirring and passing HCl gas into the mixture. The mixture was left overnight to form a precipitate at room temperature. The precipitate was filtered and recrystallized from Et_2O -hexane (1:1). The crystallized product was filtered off, washed with hexane and dried. Yield: 2.92 g (74%), m.p.: 175 °C.

Synthesis of 4,4'-thiobis(chlorophenylglyoxime) [H₄L]

A quantity of (3.97 g, 10 mmol) 4,4'-thiobis(phenylglyoxylohydroximoyl chloride) was dissolved in 30 mL of ethanol. Subsequently, solutions of (1.53 g, 22 mmol) $\text{NH}_2\text{OH}\cdot\text{HCl}$ and (1.64 g, 20 mmol) CH_3COONa (dissolved in the minimum amount of water) were added with stirring. The reaction mixture was heated for 6 h at 40 °C and then the mixture was left to stand for 5 days. The precipitate was filtered off and recrystallized from ethanol. Yield: 1.92 g (45%), m.p.: 228 °C.

Synthesis of substituted 4,4'-thiobis(aminophenylglyoximes)

The substituted 4,4'-thiobis(aminophenylglyoximes) were obtained by the reaction of amines [aniline, 4-methylaniline and 2-(aminomethyl)pyridine] with 4,4'-thiobis(chlorophenyl- glyoxime) in the presence of triethylamine. The amine (20 mmol) and triethylamine (20 mmol) dissolved in 10 mL of methanol was added dropwise to a suspension of 4,4'-thiobis (chlorophenylglyoxime) (10 mmol) in 50 mL of methanol over 15 min. The mixture was stirred for a further 5-6 h, then diluted with 150 mL of water and left to stand overnight at room temperature. The resulting precipitates were filtered and then recrystallized from methanol-water (1:4). The products were filtered, washed with water and dried.

All analytical data, colors, yields and melting points of these ligands are presented in Tables 1, 2 and 3.

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 ₁₆ H ₁₀ N ₂ O ₄ Cl ₂ S] H ₂ L	Dark yellow	175	75	48.36 (50.82)	2.52 (2.39)	7.05 (6.97)	-
[C ₁₆ H ₁₂ N ₂ O ₄ Cl ₂ S] H ₄ L	Cream	228	65	44.96 (45.08)	2.81 (2.74)	13.11 (13.05)	-
[C ₂₈ H ₂₆ N ₈ O ₄ S] H ₄ L ¹	Cream	159*	63	58.94 (58.81)	4.56 (4.47)	19.64 (19.75)	-
[C ₂₈ H ₂₈ N ₈ O ₄ SCo] [Co(H ₂ L ¹)]	Brown	220*	85	53.59 (53.67)	3.83 (3.74)	17.87 (18.07)	9.39 (9.32)
[C ₂₈ H ₂₈ N ₈ O ₆ SNi] [Ni(H ₂ L ¹)]	Red brown	251*	86	50.70 (50.84)	4.22 (4.15)	16.9 (17.03)	8.86 (8.82)
[C ₂₈ H ₂₈ N ₈ O ₄ SCu] [Cu(H ₂ L ¹)]	Dark green	217*	87	53.20 (53.16)	3.80 (3.72)	17.73 (17.64)	10.06 (9.98)
[C ₂₈ H ₂₄ N ₆ O ₄ S] H ₄ L ²	Yellow	150*	61	62.22 (62.26)	4.44 (4.35)	15.55 (15.66)	-
[C ₂₈ H ₂₂ N ₆ O ₄ SCo] [Co(H ₂ L ²)]	Brown	>300	83	56.28 (56.24)	3.67 (3.54)	14.06 (14.14)	9.87 (9.78)
[C ₂₈ H ₂₂ N ₆ O ₄ SNi] [Ni(H ₂ L ²)]	Red brown	>300	80	56.30 (56.34)	3.68 (3.59)	14.07 (14.14)	9.83 (9.78)
[C ₂₈ H ₂₂ N ₆ O ₄ SCu] [Cu(H ₂ L ²)]	Dark brown	251*	86	55.85 (55.79)	3.65 (3.68)	13.96 (13.91)	10.56 (10.39)
[C ₃₀ H ₂₈ N ₆ O ₄ S] H ₄ L ³	Yellow	177*	63	63.30 (63.19)	4.92 (4.86)	14.78 (15.09)	-
[C ₃₀ H ₂₆ N ₆ O ₄ SCo] [Co(H ₂ L ³)]	Green yellow	>300	81	57.60 (57.51)	4.15 (3.99)	13.42 (13.34)	9.43 (9.34)
[C ₃₀ H ₂₆ N ₆ O ₄ SNi] [Ni(H ₂ L ³)]	Dark brown	231*	83	57.62 (57.69)	4.16 (4.10)	13.44 (13.48)	9.39 (9.28)
[C ₃₀ H ₂₆ N ₆ O ₄ SCu] [Cu(H ₂ L ³)]	Dark brown	>300	85	57.18 (57.04)	4.12 (3.91)	13.34 (13.47)	10.09 (10.06)

*Decomposition point

Table 2. Magnetic measurements and characteristic IR bands (cm^{-1}) of the ligands and their complexes as KBr Pellets.

Compounds	μ_{eff} (B.M.)	ν (O-H)	ν (C=N)	ν (N-O)	ν (N-H)	ν (C=C)
H ₂ L	-	3256 m	1496 s	1022 s	-	1496 m
H ₄ L	-	3240 m	1597 s	994 s	-	1506 m
H ₄ L ¹	-	3256 w	1565 s	986 w	3414 m	1498 m
[Co(H ₂ L ¹)]	3.70	-	1597 s	1013 w	3362 m	1498 m
[Ni(H ₂ L ¹)]	2.86	-	1597 s	1012 w	3312 m	1498 m
[Cu(H ₂ L ¹)]	1.56	-	1597 s	1013 w	3395 m	1496 m
H ₄ L ²	-	3294 w	1596 s	959 m	3276 m	1501 m
[Co(H ₂ L ²)]	1.49	-	1594 s	1013 w	3344 w	1499 m
[Ni(H ₂ L ²)]	Dia.	-	1596 s	1012 w	3334 w	1497 m
[Cu(H ₂ L ²)]	1.12	-	1595 s	1013 w	3354 m	1499 m
H ₄ L ³	-	3328 w	1595 s	959 m	3366 m	1508 m
[Co(H ₂ L ³)]	2.80	-	1596 s	1012 w	3379 w	1504 m
[Ni(H ₂ L ³)]	Dia.	-	1594 s	1014 w	3356 w	1515 m
[Cu(H ₂ L ³)]	1.08	-	1596 s	1013 w	3371 w	1502 m

s: strong, m: medium, w: weak

Table 3. ¹H NMR spectra of the ligands in DMSO- δ^6 (ppm).

Compounds	O-H ^a	O-H ^b	C-H (arom)	C-H(alip)	N-H	Others
H ₂ L	13.61 (s, 1H)	-	7.82-7.40 (d,d J = 8.20 Hz, 4H)	-	-	-
H ₄ L	12.53 (s, 1H)	12.14 (s, 1H)	7.30-7.16 (dd, J=8.13 Hz, 4H)	-	-	-
H ₄ L ¹	11.90 (s, 1H)	10.76 (s, 1H)	7.61-6.82 (m, 8H)	4.31 (d, 2H)	8.37 - (t, J = 695 Hz, 1H)	-
H ₄ L ²	11.98 (s, 1H)	10.48 (s, 1H)	7.39-6.70 (m, 9H)	-	8.18 (s, 1H)	-
H ₄ L ³	11.96 (s, 1H)	10.35 (s, 1H)	7.39-6.69 (m, 8H)	-	7.99 (s, 1H)	2.2 (Ar-CH ₃) (s, 3H)

s: singlet, d: doublet, t: triplet, m: multiplet

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

A quantity of 1.00 mmol substituted 4,4'-thiobis(aminophenylglyoximes) was dissolved in 40 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 ethanol (95%) 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 precipitated 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 ether and dried. The polymeric metal complexes of substituted bis(aminophenylglyoxime) thioethers are insoluble in organic solvents.

The colors, yields, melting points, elemental analyses and FT-IR data of the complexes are given in Tables 1 and 2.

Results and Discussion

4,4'-Bis(chloroacetyl)diphenyl thioether was obtained by the reaction of chloroacetyl chloride with diphenyl thioether in the presence of AlCl_3 as catalyst in a Friedel-Crafts reaction¹². 4,4'-Thiobis(phenylglyoxylohydroximoyl chloride)[H_2L] was originally synthesized by following the methods described in the literature¹³. Then 4,4'-thiobis(chlorophenylglyoxime)[H_4L] and their ligands were also synthesized using the methods described in the literature^{14–15}. These reactions are shown below in Figure 1. The physical properties and spectral data of substituted 4,4'-thiobis(aminophenylglyoxime) are given in Tables 1, 2 and 3.

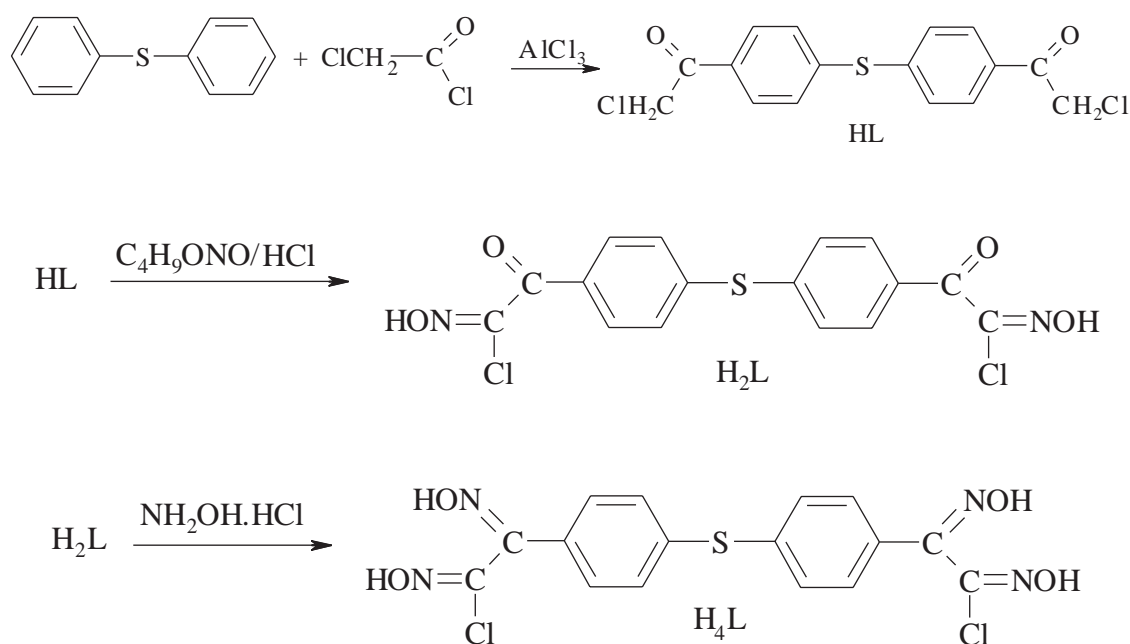


Figure 1. The synthesis of 4,4'-thiobis(phenylglyoxylohydroximoyl chloride) (H_2L) and 4,4'-thiobis(chlorophenylglyoxime) (H_4L).

We report the synthesis of 3 new substituted 4,4'-thiobis(aminophenylglyoxime), shown below in Figure 2, and the metal complexes of these compounds.

In the ^1H NMR spectra of the 4,4'-thiobis(chlorophenylglyoxime) (H_4L), 2 peaks are present for the O-H protons while the OH protons of the chloroketo oxime (H_2L) appear as a singlet. When the chemical shift values of the 2 OH groups in the 4,4'-thiobis (chlorophenylglyoxime) and substituted 4,4'-thiobis(aminophenylglyoximes) are compared, the ones at the lower field quite closely resemble each other (11.98-12.53 ppm) while a considerable difference was observed for those at the higher field (10.35-12.14 ppm)^{4–5}. The NH protons neighboring the oxime groups were observed at 7.99-8.37 ppm and the aromatic C-H protons at 6.69-7.82 ppm. These values are given in Table 3.

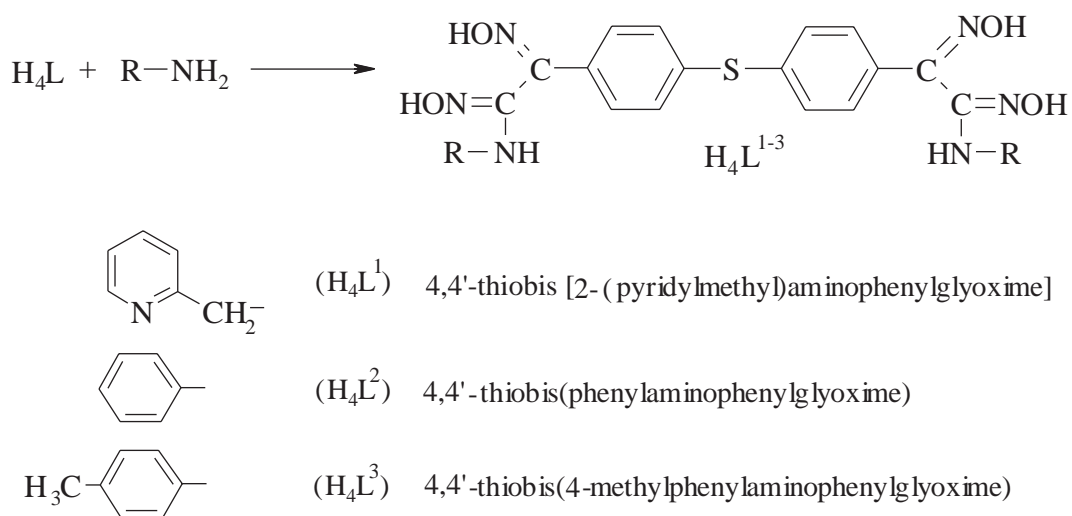


Figure 2. The structure of the ligands.

The Cu(II), Ni(II) and Co(II) complexes of the substituted 4,4'-thiobis(aminophenyl- glyoximes) were obtained in ethanol by the addition of sufficient 1% NaOH to increase the pH to 5.5-6.0. The structures of the complexes are shown in Figures 3 and 4; their colors, melting points and elemental analysis results are given in Table 1, the and FT-IR data and magnetic measurements are given in Table 2. The structure of the complexes was characterized by FT-IR, elemental analysis and magnetic measurements. ¹H NMR spectra of these complexes could not be taken because of their very low solubility in organic solvents.

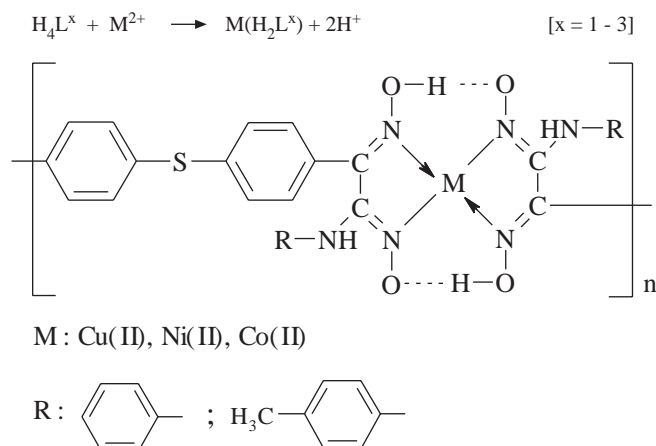


Figure 3. Suggested structures of the square-planar polymeric metal complexes of substituted bis(aminophenylglyoxime)thioethers.

In the FT-IR spectra of ligands (as KBr pellets), bands at 3276-3414, 3256-3328, 1496-1597 and 959-1022 cm⁻¹ were assigned to NH, O-H, C=N and N-O stretching vibrations, respectively. A downward shift (for H₄L¹) of 32 cm⁻¹ for the C=N absorption in the complexes indicated coordination through the nitrogen atoms¹⁶. Bands appearing at 2359-2365 cm⁻¹ in the compounds indicate that there are intramolecular H-bridges. In the FT-IR spectra of the complexes, the shift of the vibration corresponding to the N-O band to a higher frequency indicates the formation of coordination bonds between the metal and the nitrogen atoms of the dioximes. FT-IR data of the ligands and their complexes are given in Table 2.

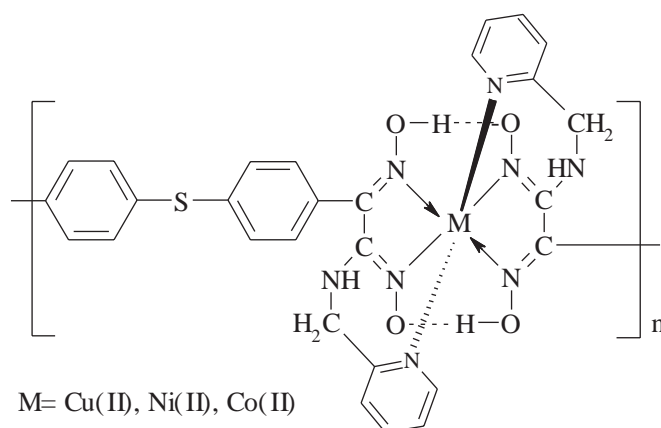


Figure 4. Suggested structure of the octahedral polymeric metal complexes of 4,4'-thiobis[2-(pyridylmethyl)aminophenylglyoxime].

The elemental analyses of the complexes indicated that the metal-ligand ratios are 1:1 in the polymeric metal complexes. The molecular weights of polymeric metal complexes could not be determined because of their insolubility in organic solvents. According to the FT-IR data, elemental analyses results and magnetic susceptibility measurements, 4,4'-thiobis(phenyl-aminophenylglyoxime) and 4,4'-thiobis(4-methylphenylaminophenylglyoxime) complexes have a square-planar structure while 4,4'-thiobis[(2-pyridylmethyl)aminophenylglyoxime] complexes have an octahedral structure. Magnetic susceptibility measurements of the complexes provide information regarding their structures and are shown in Table 2. The Ni(II) complexes are diamagnetic except for the Ni(II) complex of 4,4'-thiobis[2-(pyridylmethyl)aminophenylglyoxime]. This Ni(II) complex is paramagnetic with a magnetic susceptibility value of 2.86, which is in agreement with the 2-spin value of 2.83 B.M. According to the elemental analysis and inductively coupled plasma (ICP-AES) results, this Ni(II) complex also has 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 configuration¹⁷⁻¹⁸. The Cu(II) and Co(II) complexes are paramagnetic with magnetic susceptibility values of 1.08-1.56 and 1.49-3.70 B.M., respectively. The room temperature magnetic moments of the copper(II) complexes are in the 1.08-1.56 B.M. range (Table 2), which is well below the spin-only value of 1.73 B.M., indicating spin-exchange interaction between copper(II) ions¹⁹.

The above values of FT-IR, ¹H NMR, elemental analysis and magnetic susceptibility are in agreement with those previously reported, particularly those of substituted bis(aminophenylglyoxime) methanes²⁰ and other aminoglyoximes^{6,21-23}.

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