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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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# Syntheses, Structural Characterization, and Thermal Properties of New 1,2,3,4-Tetrahydroquinazoline Ligands and Their Co(III) Complexes

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# Syntheses, Structural Characterization, and Thermal Properties of New 1,2,3,4-Tetrahydroquinazoline Ligands and Their Co(III) Complexes

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In this study, new heterocyclic ligands, 2-(3-chloro-phenyl)-1,2,3,4-tetrahydro-quinazoline-2-carbaldehyde oxime,(HL<sup>1</sup>) and 2-(3-bromo-phenyl)-1,2,3,4-tetrahydro-quinazoline-2-carbaldehyde oxime,(HL<sup>2</sup>), and Co(III) complexes of their open-chain tautomer,(HL<sup>1/</sup> and HL<sup>2/</sup>), containing oxime, imine, and amine donor groups resulting from the reactions with Co(II) ion have been synthesized and characterized by spectral methods, elemental analysis, magnetic susceptibility, and thermal analysis (TG, DTG, and DTA) techniques. The obtained results show that the ligands undergo a ring-opening reaction upon complexation with Co(III) ion. The analyses confirmed the following molecular formulae:  $[Co(L^{1\prime})_2]Cl.H_2O$  and  $[Co(L^{2\prime})_2]Cl.H_2O$ .

Keywords Amine–imine–oxime, Co(III) complex, 2-(3-bromophenyl)-1,2,3,4-tetrahydro-quinazoline-2-carbaldehyde oxime, 2-(3-chloro-phenyl)-1,2,3,4-tetrahydroquinazoline-2-carbaldehyde oxime

# INTRODUCTION

Quinazoline derivatives have drawn much attention owing to their various pharmacological properties. In the literature, there are many studies relating to synthesis and pharmacological properties of quinazoline derivatives.<sup>[1-4]</sup> However, there are very few studies in the literature relating to coordination compounds of quinazoline derivatives.<sup>[5-14]</sup> In one of these studies, a new fluorescent chemosensor for sensing Co(II) using di(2picolyl)amino as a recognition group and quinazoline as a reporting group has been synthesized and characterized by Luo and co-workers.<sup>[15]</sup>

1,2,3,4-Tetrahydroquinazoline oximes which are quinazoline derivatives, are composed of two fused six-membered simple rings, a benzene ring and a hexahydropyrimidine ring, and an oxime group. The formation of 1,2,3,4-tetrahydroquinazoline

oxime is a synthesis of a imine oxime from carbonyl oxime and 2-aminobenzylamine;<sup>[16–19]</sup> there is a ring-chain tautomeric equilibrium between the tetrahydroquinazoline and the imines.<sup>[14,20–22]</sup> According to García-Deibe and co-workers, the tetrahydroquinazoline compound is the most stable form of the two tautomers, and the ring-chain tautomerism of a 2-aryl-1,2,3,4-tetrahydroquinazoline which can be exploit to induce reversible changes in the aminal–imine equilibrium, as desired, by coordination of a suitable metal ion.<sup>[14]</sup>

In earlier articles, we described the synthesis and characterization of the 1,2,3,4-tetrahydroquinazoline oximes and their complexes.<sup>[17–19]</sup> In this work, we have expanded the synthesis and characterization studies of 1,2,3,4-tetrahydroquinazoline oximes and their complexes. New heterocyclic ligands, 2-(3chloro-phenyl)-1,2,3,4-tetrahydro-quinazoline-2–carbaldehyde oxime,(HL<sup>1</sup>) and 2-(3-bromo-phenyl)-1,2,3,4-tetrahydroquinazoline-2-carbaldehyde oxime,(HL<sup>2</sup>), and complexes of their open-chain tautomer, (HL<sup>1</sup> and HL<sup>2</sup>), with Co(III) ion were synthesized and characterized by spectral methods, elemental analysis, magnetic susceptibility, and thermal analyses.

#### **EXPERIMENTAL**

### **Materials and Measurements**

All chemicals and solvents were purchased from Merck, Aldrich, or Lachema and were used without further purification.

The <sup>1</sup>H NMR and <sup>13</sup>C NMR solution spectra were recorded at 25°C on a Varian Mercury Plus 400 MHz spectrometer, utilizing deuterated dimethylsulfoxide (DMSO-d<sub>6</sub>) as a solvent. FT-IR spectra were recorded in the 4000–400 cm<sup>-1</sup> region with a Thermo-Nicolet 6700 Fourier-Transform Infrared Spectrophotometer by using KBr pellets. Thermal analysis curves (TG, DTG, and DTA) were obtained using a Seiko Exstar 6200 thermal analyzer in a dynamic dry air atmosphere at a heating rate of 10°C min<sup>-1</sup> in the temperature range of 25 to 950°C using platinum crucibles. C, H, and N microanalyses and mass spectra were carried out at the Technical and Scientific Research Council of Turkey, TUBITAK Bursa Test and Analysis Laboratory.

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SCH. 1. Synthesis of the HL<sup>n</sup>.

Magnetic susceptibility measurements were performed at room temperature with a Sherwood Scientific MK1 model Magnetic Susceptibility Balance.

## Preparation of the α-Carbonyl Oximes

 $\alpha$ -Carbonyl oximes were prepared according to a literature method<sup>[23]</sup> with little modification. Nitrosation of 1-(3-chlorophenyl)-ethanone or 1-(3-bromo-phenyl)-ethanone with butyl nitrite afforded the corresponding  $\alpha$ -carbonyl oximes. Structures of the  $\alpha$ -carbonyl oximes were inferred from its FT-IR and NMR spectral data.

(3-Chloro-Phenyl)-Oxo-Acetaldehyde Oxime, (3-ClINAP). FT-IR (KBr pellet,  $\nu$  cm<sup>-1</sup>): 3244 (s, O–H); 2985 (w, H–C=N); 1628 (s, sh, C-O); 1573 (sh, C=N<sub>oxime</sub>); 1003 (s, sh, N–O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ ppm J Hz): 12.85 (s, OH, 1H); 7.99 (s, HC=N, 1H); 7.97 (s, H<sub>aromatic</sub>, 1H), 7.89–7.86 (m, H<sub>aromatic</sub>, 1H), 7.72–7.70 (m, H<sub>aromatic</sub>, 1H), 7.55 (t, J = 8, H<sub>aromatic</sub>, 1H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ ppm): 188.40 (C=O); 148.27 (C=N<sub>oxime</sub>); 138.31, 133.51, 133.21, 130.87, 129.86, 128.61 (C<sub>aromatic</sub>).

(3-Bromo-Phenyl)-Oxo-Acetaldehyde Oxime, (3-BrINAP). FT-IR (KBr pellet,  $\nu$  cm<sup>-1</sup>): 3253 (s, O–H); 3003 (w, H–C=N); 1642 (s, sh, C=O); 1565 (sh, C=N<sub>oxime</sub>); 998 (s, sh, N–O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$  ppm J Hz): 12.84 (s, OH, 1H); 7.98 (s, HC=N, 1H); 8.10 (s, H<sub>aromatic</sub>, 1H), 7.92–7.90 (m, H<sub>aromatic</sub>, 1H), 7.85–7.82 (m, H<sub>aromatic</sub>, 1H), 7.48 (t, J = 8, H<sub>aromatic</sub>, 1H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>,  $\delta$  ppm): 188.33 (C=O); 148.29 (C=N<sub>oxime</sub>); 138.51, 136.09, 132.73, 131.11, 128.96, 121.93 (C<sub>aromatic</sub>).

# **Preparation of the Ligands**

 $HL^1$  and  $HL^2$  were prepared by the usual condensation method. A solution of 2-aminobenzylamine (2-ABA) (5.00 mmol, 0.61 g) in 5 mL of absolute ethanol was added dropwise to a solution of 3-CIINAP (5.00 mmol, 0.92 g) or 3-BrINAP (5.00 mmol, 1.15 g) in 15 mL of absolute ethanol. The reaction mixture was stirred for 2 h at room temperature and left for a few days at room temperature. The reaction product was filtered, washed with cold ethanol and finally dried on air (Scheme 1).

2-(3-Chloro-Phenyl)-1,2,3,4-Tetrahydro-Quinazoline-2-

Carbaldehyde Oxime,  $(HL^1)$ . Yield: 0.87 g, 60.4% (white crystals). m.p.: 158°C (DTA<sub>max</sub>, decomposition point). Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>N<sub>3</sub>OCl (287.75 g mol<sup>-1</sup>) (%): C, 62.61; H, 4.90; N, 14.60. Found: C, 62.18; H, 4.57; N, 14.60. FT-IR (KBr pellet,  $\nu$  cm<sup>-1</sup>): 3406, 3263 (s, sh, N–H); 2963 (H–C=N); 2764 (b, N····H-O-); 1607 (sh, C=N<sub>oxime</sub>); 944 (s, sh, N-O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ ppm J Hz): 10.94 (s, -OH, 1H); 7.58  $(t, J = 1.6, H_{aromatic}, 1H); 7.52 (dt, J = 8.0; 1.2, H_{aromatic})$ 1H); 7.44 (s, HC=N, 1H); 7.35 (t, J = 7.8, H<sub>aromatic</sub>, 1H); 7.31–7.28 (m,  $H_{aromatic}$ , 1H); 6.92 (t, J = 7.6,  $H_{aromatic}$ , 1H); 6.73 (d, J = 7.8, H<sub>aromatic</sub>, 2H); 6.78 (s, N<sub>1</sub>H, 1H); 6.47 (dt, J= 7.4, 1.2, H<sub>aromatic</sub>, 1H); 3.70 (dd,  $J = 16.8, 5.6, -CH_2-N$ , 1H); 3.46–3.40 (m, -CH<sub>2</sub>-N, 1H); 3.31–3.24 (m, N<sub>3</sub>H, 1H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>,  $\delta$  ppm): 152.44 (C=N<sub>oxime</sub>); 146.53, 143.04, 133.22, 130.42, 127.86, 127.67, 127.23, 126.61, 125.97, 120.29, 116.58, 114.75 ( $C_{aromatic}$ ); 70.93 (<sup>Ph</sup>>C<); 41.93 (-CH<sub>2</sub>-N). *m*/*z*: 287.6 [HL<sup>1</sup>]<sup>+</sup>.

2-(3-Bromo-Phenyl)-1,2,3,4-Tetrahydro-Quinazoline-2-Carbaldehyde oxime, (HL<sup>2</sup>). Yield: 0.98 g, 59.0% (white crystals). m.p.: 159°C (DTA<sub>max</sub>, decomposition point). Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>N<sub>3</sub>OBr (332.20 g mol<sup>-1</sup>) (%): C, 54.23; H, 4.25; N, 12.65. Found: C, 53.95; H, 3.84; N, 12.31. FT-IR (KBr pellet,  $\nu$  cm<sup>-1</sup>): 3408, 3264 (s, sh, N–H); 2962 (H–C=N); 2765 (b, N····H-O-); 1606 (sh, C=N<sub>oxime</sub>); 943 (s, sh, N-O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$  ppm, J Hz): 10.95 (s, OH, 1H); 7.72 (t, J = 1.6, H<sub>aromatic</sub>, 1H); 7.56 (d, J = 1.6, H<sub>aromatic</sub>, 1H); 7.44 (s, HC=N, 1H); 7.42 (d, J = 3.2, H<sub>aromatic</sub>, 1H); 7.29 (t, J = 7.8, H<sub>aromatic</sub>, 1H); 6.92 (t, J = 7.8, H<sub>aromatic</sub>, 1H); 6.80 (s, N<sub>1</sub>H, 1H); 6.73 (t, J = 8, H<sub>aromatic</sub>, 2H); 6.46 (dt, J = 7.2, 1.2,  $H_{\text{aromatic}}$ , 1H); 3.70 (dd, J = 16.8, 5.6,  $-CH_2-N$ , 1H); 3.46-3.40 (m,  $-CH_2-N$ , 1H); 3.29-3.25 (m, N<sub>3</sub>H, 1H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ ppm): 152.47 (C=N<sub>oxime</sub>); 146.76, 143.02, 130.73, 130.55, 127.24, 127.00, 125.97, 121.89, 120.28,



X: Cl for  $HL^1$ , Br for  $HL^2$ 

SCH. 2. Synthesis of the Co(III) complexes.

116.57, 114.74 (C<sub>aromatic</sub>); 70.89 (<sup>Ph</sup>>C<); 41.92 (-CH<sub>2</sub>-N). m/z: 331.6 [HL<sup>2</sup>]<sup>+</sup>.

# General Procedure for Preparation of the Complexes

A solution of  $CoCl_2 \cdot 6H_2O$  (0.75 mmol, 0.178 g) in ethanol (5 mL) was added dropwise while stirring at room temperature to a solution of HL<sup>n</sup> (1.50 mmol, 0.432 g for HL<sup>1</sup> and 0.498 g for HL<sup>2</sup>) in ethanol (30 mL). Air oxidation was achieved by stirring vigorously in air for 5 h. After 5 h, the precipitated orange-colored compound was filtered, washed with cold ethanol several times, and dried on air (Scheme 2).

*Bis*{(2-*Amino-Benzylimino*)-(3-*Chloro-Phenyl*)-*Acetaldehy de* Oximato}*Cobalt*(*III*) *Chloride Monohidrate*,  $[Co(L^{1'})_2]$ *Cl·H*<sub>2</sub>O, (1). Yield: 0.27 g, 52.4%. m.p.: 217°C (DTA<sub>max</sub>, decomposition point). Anal. Calcd. for C<sub>30</sub>H<sub>28</sub>N<sub>6</sub>O<sub>3</sub>Cl<sub>3</sub>Co (686.52 g mol<sup>-1</sup>) (%): C, 52.33; H, 4.10; N, 12.30. Found: C, 52.61; H, 3.67; N, 12.13. FT-IR (KBr pellet,  $\nu$  cm<sup>-1</sup>): 3431 (b, H<sub>2</sub>O); 3236, 3199 (sh, N–H); 1618 (sh, C=N<sub>imine</sub>); 1566 (sh, C=N<sub>oxime</sub>); 1041 (s, sh, N–O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ ppm, *J* Hz): 7.74–7.46 (m, H<sub>aromatic</sub>, 6H and NH<sub>2</sub>, 4H); 7.21–7.17 (m, CH<sub>aromatic</sub>, 8H); 6.92 (s, H–C=N, 2H); 6.68 (d, *J* = 11.6, H<sub>aromatic</sub>, 2H); 4.87 (d, *J* = 14, CH<sub>2</sub>, 2H); 4.71 (d, *J* = 14.4, CH<sub>2</sub>, 2H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ ppm): 173.09 (Ph–C=N); 139.46 (H–C=N); 139.00–123.04 (C<sub>aromatic</sub>); 53.80 (CH<sub>2</sub>). m/z: 632.3 [Co(L<sup>1</sup>)<sub>2</sub>]<sup>+</sup>. μ<sub>eff</sub>: diamagnetic.

Bis{(2-Amino-Benzylimino)-(3-Bromo-Phenyl)-Acetaldehyde Oximato}Cobalt(III) Chloride Monohidrate,  $[Co(L^{2'})_2]$  $JCl\cdot H_2O$ , (2). Yield: 0.42 g, 72.3%. m.p.: 214°C (DTA<sub>max</sub>, decomposition point). Anal. Calcd. for C<sub>30</sub>H<sub>28</sub>N<sub>6</sub>O<sub>3</sub>Br<sub>2</sub>ClCo (774.79 g mol<sup>-1</sup>) (%): C, 46.51; H, 3.64; N, 10.85. Found: C, 46.80; H, 3.33; N, 10.59. FT-IR (KBr pellet,  $\nu$  cm<sup>-1</sup>): 3454 (b, H<sub>2</sub>O); 3233, 3199 (sh, N–H); 1613 (sh, C=N<sub>imine</sub>); 1559 (sh, C=N<sub>oxime</sub>); 1022 (s, sh, N–O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$ ppm, J Hz): 7.85 (d, J = 7.2, H<sub>aromatic</sub>, 2H); 7.76–7.38 (m, H<sub>aromatic</sub>, 4H and NH<sub>2</sub>, 4H); 7.29–7.11 (m, H<sub>aromatic</sub>, 8H); 6.91 (s, H–C=N, 2H); 6.66 (d, J = 11.2, H<sub>aromatic</sub>, 2H); 4.86 (d, J = 14.4, CH<sub>2</sub>, 2H); 4.71 (d, J = 14.4, CH<sub>2</sub>, 2H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>,  $\delta$  ppm): 173.03 (Ph-C=N); 139.50 (H-C=N); 139.00–122.46 (C<sub>aromatic</sub>); 53.80 (CH<sub>2</sub>). *m*/*z*: 721.2 [Co(L<sup>2'</sup>)<sub>2</sub>]<sup>+</sup>.  $\mu_{eff}$ : diamagnetic.

## **RESULTS AND DISCUSSION**

The ligands HL<sup>1</sup> and HL<sup>2</sup> were synthesized by the condensation of 2-ABA with 3-CIINAP or 3-BrINAP, respectively. The addition of cobalt(II) chloride solution prepared in ethanol to an alcoholic solution of the ligands gave orange-colored complexes (Scheme 2). They were determined that cobalt(II) is becoming oxidized to cobalt(III) in the complexes. The physicochemical and spectral data of the ligands and the complexes of their imine tautomer are given in Experimental Section.

#### **Elemental Analyses and Magnetic Susceptibility**

The C, H, and N contents (both theoretically calculated values and actual values) are in reasonably good agreement with the proposed formulae. The magnetic susceptibility measurement of the cobalt(III) complexes reveal that the compounds are diamagnetic, confirming the oxidation of cobalt(II) to cobalt(III) and corresponding to low spin  $d^6$  system for Co(III) which suggest octahedral geometry.<sup>[17–19]</sup>

#### Mass Spectra

In the free ligands, the molecular ion peaks have been observed at m/z 287.6 for HL<sup>1</sup> and at m/z 331.6 for HL<sup>2</sup>. In the mass spectra of the cobalt(III) complexes, the strong peaks at m/z 632.3 and at m/z 721.2 can be related to the  $[Co(L^{1/})_2]^+$  and  $[Co(L^{2'})_2]^+$  ions, respectively.

#### IR Spectra

The FT-IR spectra of the solid form of  $HL^n$  indicate that the ligands are in ring form. There are two main features in the FT-IR spectra of the new ligands,  $HL^1$  and  $HL^2$ . The first one is the disappearance of the characteristic carbonyl group of the α-carbonyl oximes, while the second feature is the appearance of the band at ca. 1302 cm<sup>-1</sup> for HL<sup>1</sup> and HL<sup>2</sup>, which is assigned to stretching vibration of the -C-N- group and confirming the condensation reactions. The FT-IR spectra of the ligands exhibited fairly strong bands at 3408–3263 cm<sup>-1</sup> attributable to the  $\nu(N-H)$  vibrations. The oxime (-OH) stretching vibration of the ligands appeared as a broad peak maximum at 2764 cm<sup>-1</sup> for HL<sup>1</sup> and 2765 cm<sup>-1</sup> for HL<sup>2</sup>, assigned to the intramolecular hydrogen bonding vibration (N····H-O-). In the FT-IR spectra of the ligands,  $\nu(H-C=N)$ ,  $\nu(C=N_{oxime})$ , and  $\nu(N-O)$ characteristic stretching vibration bands were observed at 2963, 1607, and 944 cm<sup>-1</sup> for HL<sup>1</sup> and at 2962, 1606, and 943 cm<sup>-1</sup> for HL<sup>2</sup>. These values are in accord with those of previously reported 1,2,3,4-tetrahydroquinazoline oximes.<sup>[16–19]</sup>

In the FT-IR spectra of the Co(III) complexes, the  $\nu$ (O–H) band due to water molecule was assigned at 3600–3250 cm<sup>-1</sup>. This very broad band prohibits the appearance of other bands in the region. Regarding the FT-IR spectra of the Co(III) complexes, the stretching vibration band was determined to be caused by the imine group (–C=N) and the band corresponding to the (–C–N–) vibration of the heterocyclic ring was disappeared as results of the complexation and formation of chain form within the complexes. These results show that the ligands are converting to chain form in the Co(III) complexes and they are coordinating to the metal ion in the chain form.

Compared the FT-IR spectra of Co(III) complexes with the FT-IR spectra of free ligands the displacement of the bands to lower or upper frequencies were observed. This proofs the coordination of the ligands to the Co(III) ion. For example, when the FT-IR spectra of the complexes are compared with those of the free ligands, the  $\nu$ (C=N<sub>oxime</sub>) band is shifted to a lower frequency. This situation indicates that the oxime nitrogen must be coordinated to the metal ion. The  $\nu$ (N–O) band in the Co(III) complexes is situated at a frequency significantly higher than that of the free ligands, owing to the coordination of the N atom and the increase in bond order of the N–O bond upon deprotonation.

# <sup>1</sup>H- and <sup>13</sup>C-NMR Spectra

In the <sup>1</sup>H NMR spectra of the ligands, a singlet peak for the -OH proton of oxime group is observed at  $\delta$  10.94 ppm. The NH proton adjacent to the  $-CH_2$  group and other NH proton in the heterocyclic ring resonate at  $\delta$  3.31–3.24 ppm (1H as a multiplet) and  $\delta$  6.78 ppm (1H as a singlet) for HL<sup>1</sup> and  $\delta$  3.29–3.25 ppm (1H as a multiplet) and at  $\delta$  6.80 ppm (1H as a singlet) for HL<sup>2</sup>. The  $-CH_2$  group in the heterocyclic ring of the ligands resonates at  $\delta$  3.70 ppm and  $\delta$  3.46–3.40 ppm. The aldehyde proton adjacent to the oxime group resonates at 7.44 ppm for the ligands. The integration of the <sup>1</sup>H NMR spectra suggests the presence of a range of proton resonances between 7.72 and 6.46 ppm because of the resonance of 8 phenyl protons of the ligands.

The <sup>13</sup>C NMR spectra of the  $\alpha$ -carbonyl oximes showed a signal for the carbon atom of the carbonyl group at  $\delta$  188.40 ppm for 3-CIINAP and  $\delta$  188.33 ppm for 3-BrINAP while this was not observed in the <sup>13</sup>C NMR spectra of the HL<sup>1</sup> and HL<sup>2</sup>. In addition, the HL<sup>1</sup> and HL<sup>2</sup> ligands showed a signal corresponding to the quaternary carbon atom of the heterocyclic ring at  $\delta$  70.93 ppm and  $\delta$  70.89 ppm, respectively, suggesting that the 1,2,3,4-tetrahydroquinazoline ring is formed.<sup>[16–19]</sup> The carbon atom of the oxime group was observed at  $\delta$  152.44 ppm for HL<sup>1</sup> and  $\delta$  152.47 ppm for HL<sup>2</sup>. The <sup>13</sup>C NMR spectra of the ligands displayed a range of aromatic carbon resonances between  $\delta$  146.76 and 114.74 ppm. As for the carbon atom of  $-CH_2-$  group in HL<sup>1</sup> and HL<sup>2</sup>, it was resonated at  $\delta$  41.93 ppm and  $\delta$  41.92 ppm, respectively.

A comparison of the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of these ligands with those of the Co(III) complexes confirms the coordination of the aniline-type chain form of the ligands. In the <sup>1</sup>H NMR spectra of the Co(III) complexes, there is no OH peak belonging to the oxime group, providing evidence for deprotonation of the ligands. The chemical shift belonging to the -NHadjacent to the  $-CH_2$  group in the HL<sup>1</sup> and HL<sup>2</sup> disappeared from the <sup>1</sup>H NMR spectra of the Co(III) complexes. After the complexation, in the integrated <sup>1</sup>H NMR spectra of the Co(III) complexes, the observed proton resonances at ca.  $\delta$  7.5 ppm are due to the presence of the  $-NH_2$  groups. The peaks were assigned by the formation of the aniline-type chain form in the Co(III) complexes (Scheme 2).

In the Co(III) complexes, the peaks due to the H–C=N group and methylene group of the ligands showed an upfield shift and a downfield shift upon complexation with Co(III), respectively.<sup>[17–19]</sup> These findings confirm that the nitrogen atoms of the oxime group and imine group are coordinated to the Co(III) ion.

The chemical shift due to the quaternary carbon atom in the ligands disappeared from the <sup>13</sup>C NMR spectra of the Co(III) complexes. However, after complexation a new resonance at  $\delta$  ca. 173 ppm was observed. The new resonance shows us that the heterocyclic ring of the ligands was opened during the complexation and the aniline-type chain form occurred in the Co (III) complexes.<sup>[17–19]</sup> The chemical shifts belonging to the carbon atoms of oxime group and methylene group in the ligands showed an upfield shift and a downfield shift on complexation with Co(III). These results demonstrate the involvement of the oxime nitrogen and the nitrogen adjacent to the  $-CH_2$  group in coordination.

### **Thermal Analyses**

Thermal behaviors of the ligands and Co(III) complexes have been investigated using thermal analysis techniques. The thermal stability data are listed in Table 1. The ligands are stable up to ca. 130°C and then decompose in three separate temperature regions. Decompositions are completed at 618°C for the ligands (Figures 1 and 2).

Compound	Temperature		Total weight loss	Colculated %	Assignment
Compound	Tange, C	DIA <sub>max</sub> , C	Found, 70	Calculated, %	Assignment
	138-186	157 (-)	15.9	*	**
HL <sup>1</sup>	186-439	347 (DTG <sub>max</sub> )	61.4	*	**
	439-618	570 (-)	100	100	_
	25-198	82 (+)	2.4	2.6	$[Co(L^{1'})_2]Cl$
$[Co(L^{1'})_2]Cl\cdot H_2O$	198-232	217 (-)	19.5	*	**
	232-684	624 (-)	88.5	*	Co <sub>3</sub> O <sub>4</sub> /CoO
	684–942	927 (+)	89.4	89.1	CoO
	130-178	157 (-)	11.2	*	**
HL <sup>2</sup>		$291(DTG_{max})$			
	178-425	,	51.9	*	**
		365 (DTG <sub>max</sub> )			
		550 (-)			
	425-618		100	100	_
		593 (-)			
	25-172	78 (+)	2.2	2.3	$[Co(L^{2'})_2]Cl$
$[Co(L^{2'})_2]Cl\cdot H_2O$	172-228	214 (-)	17.9	*	**
		643 (-)			
	228-720		90.4	*	Co <sub>3</sub> O <sub>4</sub> /CoO
		690 (-)			
	720–948	922 (+)	91.1	90.3	CoO

 TABLE 1

 TG-DTA data of the ligands and their Co(III) complexes

(+): endothermic, (-): exothermic, \*: not computed, \*\*: unknown.

TG, DTG, and DTA curves for the Co(III) complexes are given in Figures 3 and 4. It is rather difficult to comment on the mass loss calculated in the thermal analysis of these complexes because of the lack of smooth plateaux. However, DTA curves indicate that the decomposition can occur in four steps between 25 and 950°C. The first mass loss corresponds to the removal of the hydrated water from the complex (1) between 25 and 198°C. The loss of mass found from TG curve is equal to 2.4% (calcd. 2.6%) which corresponds to the release of one water molecule. On heating the complex (2) also releases one water molecule in the range of 25 to  $172^{\circ}$ C. The loss of weight found from TG curve is 2.2% and calculated as 2.3%. This value confirms the release of one water molecule. The following two exothermic steps are related to the release of HL<sup>n</sup> ligands and counter ion for the complexes. The mixture of Co<sub>3</sub>O<sub>4</sub>/CoO is caused by the removal of the organic ligands and counter ion. The decomposition product Co<sub>3</sub>O<sub>4</sub> is converted to CoO between 684 and 942°C for (1) (DTA<sub>max</sub>: 927°C) and between 720 and



FIG. 1. TG, DTG, and DTA curves of HL<sup>1</sup>.



FIG. 2. TG, DTG, and DTA curves of HL<sup>2</sup>.



FIG. 3. TG, DTG, and DTA curves of  $[Co(L^{1'})_2]Cl \cdot H_2O$ .



FIG. 4. TG, DTG, and DTA curves of  $[Co(L^{2'})_2]Cl \cdot H_2O$ .

948°C for (2) (DTA<sub>max</sub>: 922°C). These findings demonstrate that the organic ligand acts as a reducing agent during thermal decomposition. The final decomposition product of the complexes is CoO [found: 10.6%, calcd.: 10.9% for (1) and found: 8.9%, calcd.: 9.7% for (2)].

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