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Synthesis and Characterization of New Tridentate Iminooxime Ligands and Their Co(III) Complexes

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In this study, (hydroxyimino)(2-phenyl(1,2,3,4-tetrahydroquinazolin-2-yl))methane (H_2L^1) and (hydroxyimino)(2-(2-thienyl)(1,2,3,4-tetrahydroquinazolin-2-yl))methane (H_2L^2) were synthesized by the condensation of 2-(hydroxyimino)-1-phenylethan-1-one (INAP) and 2-(hydroxyimino)-1-(2-thienyl)ethan-1-one (INAT) with 2-aminobenzylamine (2-ABA). Complexes of these ligands with Co^{3+} were prepared with a metal:ligand ratio of 1:2. The ligands and their complexes were elucidated on the basis of elemental analyses, AAS, FT-IR, ^{1}H- and ^{13}C-NMR spectra, mass spectra, magnetic susceptibility measurements, and molar conductivity.

Key Words: 1,2,3,4-tetrahydroquinazoline, tetrahydroquinazoline oxime, iminooxime, Schiff bases, cobalt(III) complexes.

Introduction

The many and varied biological properties of quinazolines have been widely studied in recent years.[1−4] Some quinazolines have been identified as inhibitors of cyclin-dependent kinases by Sielecki et al.[5] Many quinazoline derivative compounds exhibit biological activity.[6] Tetrahydroquinazolines have been extensively studied recently.[7−11] The ring-chain tautomerism of 2-aryl-1,2,3,4-tetrahydroquinazolines has been found in compounds formed by the reaction of 2-aminobenzylamine and the corresponding aldehydes.[10] In addition, Ni(II) complex of 2-phenyl-2-(1-hydroxyiminoethyl)-1,2,3,4-tetrahydroquinazoline as a ligand has been reported.[12]

The formation of Schiff bases by the condensation of amines with aldehydes or ketones is well known.[13−15] Schiff base and oxime compounds have been extensively studied because of their biological and structural importance arising from their specific and selective reactions with metal ions.[16] Many Schiff base derivatives containing substituted oxime have been synthesized, characterized in detail, and used

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for complexation with some transition metal ions in the literature.[17,18] α-Iminooximes are species like these ligands.[14,15,19–23] Since cobalt complexes are present in active sites of several important classes of metalloproteins, their study is of great interest in various aspects of chemistry.[24–26] As models for coenzyme B_{12}, cobaloximes have been subjected to extensive studies including their electrochemical and structural properties.[27]

In this study, new tetrahydroquinazoline derivatives that are oxime ligands were prepared and α-iminooxime coordination compounds were also synthesized resulting from the reaction between these compounds and cobalt(II) salt. The compounds were characterized by elemental analyses, mass spectroscopy, AAS, FT-IR, ^{1}H-NMR, ^{13}C-NMR, magnetic susceptibility measurements, and molar conductivity.

Experimental

Materials and measurements

2-(Hydroxyimino)-1-phenylethan-1-one (INAP) was prepared according to literature methods.[28] 2-(Hydroxyimino)-1-(2-thienyl)ethan-1-one (INAT) was prepared as described by Chhakkar and Kakkar.[29] All reagents were purchased from Merck, Aldrich, or Lachema and were used without further purification. Melting points were determined on a BÜCHI B-540 digital melting point apparatus and are uncorrected. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature. The conductometric measurements were carried out with a WTW inoLab 730 conductivity meter. ^{1}H-NMR and ^{13}C-NMR solution spectra in DMSO-D_6 were recorded at 298 K on a Varian Mercury Plus 400 MHz spectrometer with TMS as reference. The IR spectra were recorded on a Thermo-Nicolet 6700 Fourier-Transform Infrared Spectrometer in the 400-4000 cm^{-1} range using KBr disks. Metal analyses were performed using an ATI-UNICAM 929 AAS spectrometer. The elemental microanalyses and mass spectra were carried out at the Scientific and Technological Research Council of Turkey (TÜBİTAK).

Preparation of ligands

(Hydroxyimino)(2-phenyl(1,2,3,4-tetrahydroquinazolin-2-yl))methane, H_2L^1, and (hydroxyimino)(2-(2-thienyl)(1,2,3,4-tetrahydroquinazolin-2-yl))methane, H_2L^2, were prepared by the usual condensation method (Figure 1). 2-Aminobenzylamine (1.2220 g, 10 mmol) was dissolved in absolute ethanol (10 mL) and added to solutions of 2-(hydroxyimino)-1-phenylethan-1-one (1.4930 g, 10 mmol) or 2-(hydroxyimino)-1-(2-thienyl)ethan-1-one (1.5500 g, 10 mmol) in 10 mL of absolute ethanol. The reaction mixture was stirred for 2 h and then left for 2 days at room temperature. The crystalline reaction product was filtered and washed with cold ethanol.

(Hydroxyimino)(2-phenyl(1,2,3,4-tetrahydroquinazolin-2-yl))methane, H_2L^1, is soluble in acetone, THF, DMSO, DMF, dioxane, and pyridine, and is slightly soluble in $CHCl_3$, EtOH, and MeOH. Yield: 1.8698 g (73.81%), mp: 142.0 °C (decomposition point).

(Hydroxyimino)(2-(2-thienyl)(1,2,3,4-tetrahydroquinazolin-2-yl))methane, H_2L^2, is soluble in acetone, THF, DMSO, dioxane, and MeOH, and is slightly soluble in $CHCl_3$ and EtOH. Yield: 0.2400 g (9.25%), mp: 135.7 °C (decomposition point).

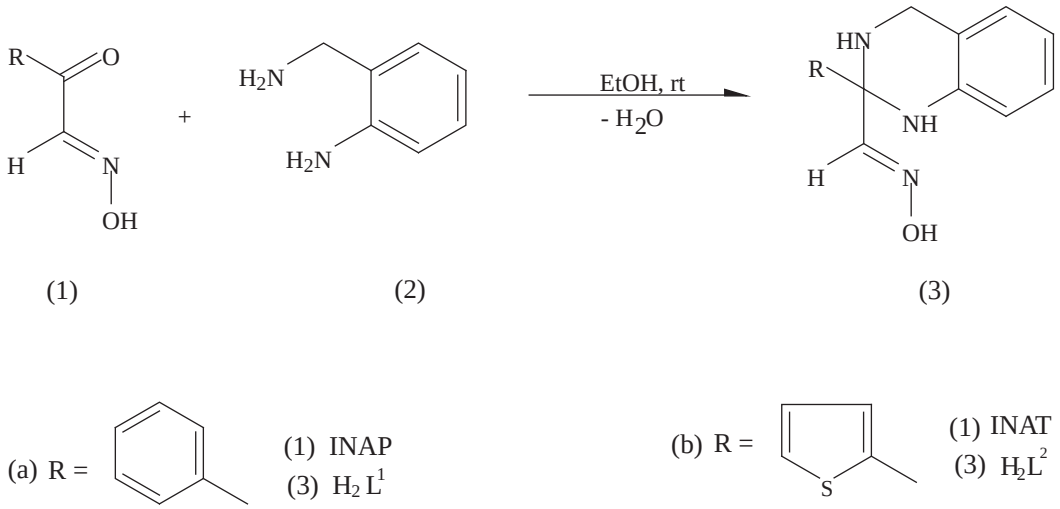

Figure 1. Preparation of the ligands. (a) (1) : 2-(Hydroxyimino)-1-phenylethan-1-one (INAP), (3): (Hydroxyimino)(2-phenyl(1,2,3,4-tetrahydroquinazolin-2-yl))methane (H_2L^1), (b) (1): 2-(hydroxyimino)-1-(2-thienyl)ethan-1-one (INAT), (3) (Hydroxyimino)(2-(2-thienyl)(1,2,3,4-tetrahydroquinazolin-2-yl))methane (H_2L^2).

Preparation of complexes

$CoCl_2.6H_2O$ (0.0595 g, 0.25 mmol) was dissolved in absolute ethanol (15 mL) and added to solutions of (hydroxyimino)(2-phenyl(1,2,3,4-tetrahydroquinazolin-2-yl))methane (0.1267 g, 0.5 mmol) or (hydroxyimino) (2-(2-thienyl)(1,2,3,4-tetrahydroquinazolin-2-yl))methane (0.1297 g, 0.5 mmol) in 15 mL of absolute ethanol. Air-oxidation was achieved by stirring vigorously in air for 1 h and 30 min to 2 h. An orange precipitate formed approximately 15 min later (Figure 2). These complexes were filtered and washed with water several times, and dried at room temperature.

$[CoL^1(HL^1)].H_2O$ is soluble in $CHCl_3$, MeOH, and DMSO and is slightly soluble in acetone, DMF, and dioxane. Yield: 0.0900 g (62.03%), mp: 230.9 °C (decomposition point).

$[CoL^2(HL^2)].H_2O$ is soluble in $CHCl_3$, MeOH, and DMSO and is slightly soluble in acetone and pyridine. Yield: 0.1383 g (93.32%), mp: 231 °C (decomposition point).

Results and Discussion

The desired substituted (hydroxyimino)(2-phenyl(1,2,3,4-tetrahydroquinazolin-2-yl))methane (H_2L^1) or (hydroxyimino)(2-(2-thienyl)(1,2,3,4-tetrahydroquinazolin-2-yl))methane (H_2L^2) was obtained by the reaction of 2-aminobenzylamine (2-ABA) with 2-(hydroxyimino)-1-phenylethan-1-one (INAP) or 2-(hydroxyimino)-1-(2-thienyl)ethan-1-one (INAT) in absolute ethanol solution in a single step (Figure 1). The addition of cobalt(II) chloride solution prepared in ethanol to an alcoholic solution of the ligands gave orange colored complexes by air oxidation (Figure 2). Numerous efforts to crystallize Co(III) complexes of the tetrahydroquinazoline oxime ligands failed.

The metal to ligand ratio was found to be 1:2 by elemental analyses and mass spectra. The analytical and physical data of tetrahydroquinazoline oximes and their Co(III) complexes are given in Table 1.

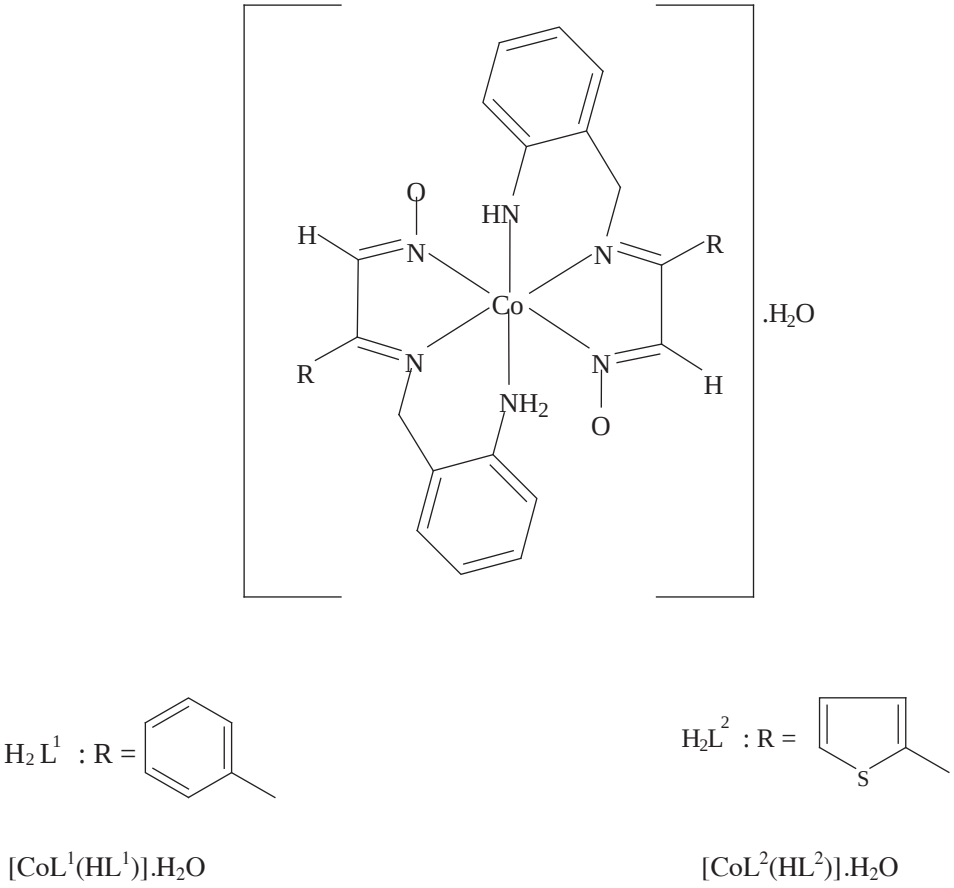

Figure 2. Structures of Co(III) complexes.

Table 1. Analytical and physical data of the tetrahydroquinazoline oximes and their Co(III) complexes.

Compound			Found (Calculated)				Λ_M(cm^2	
Molecular Formula	Color	Mol. wt.	C	H	N	Co	Ω^{-1}mol^{-1})	μ_{eff}(BM)
H_2L^1	White	253.31	70.89	6.09	16.56	–	–	–
$C_{15}H_{15}N_30$			(71.12)	(5.97)	(16.59)			
$[CoL^1(HL^1)].H_2O$	Orange	580.55	62.24	4.92	14.44	9.74	25.93	0.43
$C_{30}H_{29}N_6O_3Co$			(62.07)	(5.04)	(14.48)	(10.15)		
H_2L^2	White	259.36	60.44	4.84	16.40	–	–	–
$C_{13}H_{13}N_3SO$			(60.20)	(5.05)	(16.20)			
$[CoL^2(HL^2)].H_2O$	Orange	592.65	52.82	4.04	13.99	9.74	17.91	0
$C_{26}H_{25}N_6O_3S_2Co$			(52.69)	(4.25)	(14.18)	(9.95)		

Conductance measurements

The molar conductance values at room temperature of the synthesized cobalt(III) complexes in 1×10^{-3} M solution in absolute ethanol are included in Table 1. Conductance measurements indicate the non-electrolytic nature of these compounds.[30]

Magnetic susceptibility

Magnetic measurements were also obtained in order to obtain information on their probable geometries. The room temperature magnetic moments of the synthesized cobalt(III) complexes are incorporated into Table 1. They gave moment values of 0.43 and 0 BM for $[CoL^1(HL^1)].H_2O$ and $[CoL^2(HL^2)].H_2O$, respectively. These observed magnetic moments are regarded to be low enough to enable us to assume that the complexes are diamagnetic, low-spin type.[26]

Mass spectral studies

An attempt was made to determine the molecular masses of the H_2L^1 and H_2L^2 ligands and their cobalt(III) complexes by means of LC-mass spectral studies. In the free ligands, the molecular ion peaks, $[H_2L^n + 1]^+$ (n: 1 or 2), were observed at m/z 253.8 and 259.7. In the spectra of the cobalt(III) complexes, the strong peaks at m/z 562.9 and 574.7 can be related to the $([CoL^1(HL^1)] + 1)^+$ and $([CoL^2(HL^2)] + 1)^+$ ions, respectively.

Infrared spectra

IR spectral bands of the 2-ABA,[31] INAP,[32] INAT,[29] tetrahydroquinazoline oxime ligands H_2L^1 and H_2L^2 and their complexes $[CoL^1(HL^1)].H_2O$ and $[CoL^2(HL^2)].H_2O$ are presented in Table 2. (Hydroxyimino)(2-phenyl(1,2,3,4-tetrahydroquinazolin-2-yl))methane contains 4 potential donor sites: (1) The tetrahydroquinazoline ring nitrogen-1; (2) the tetrahydroquinazoline ring nitrogen-3; (3) the oxime oxygen; and (4) the oxime nitrogen (Figure 3). The other ligand (hydroxyimino)(2-(2-thienyl)(1,2,3,4-tetrahydroquinazolin-2-yl))methane contains an additional donor site, the thiophene sulfur. In these ligands the functional groups N-H, O-H, C=N, and N-O are readily identified from the infrared spectra. The spectra of tetrahydroquinazoline compounds exhibited fairly strong bands at 3261-3399 cm^{-1} attributable to the ν(N-H) vibration.[7] The ν(O-H) band assigned to the stretching hydrogen motions in the intramolecular O–H− − −N hydrogen bonds appears broadened with a maximum in the range 2764-2768 cm^{-1}. In the IR spectra of the α-carbonyl oxime derivatives INAP and INAT, the υ(C=O) stretching frequency of the carbonyl group appears in the 1680-1594 cm^{-1} range but disappears in the case of the tetrahydroquinazoline oximes H_2L^1 and H_2L^2, which is evidence for the formation of new ligands. The bands observed at 1606 cm^{-1} and 947-937 cm^{-1} were attributed to the oxime ν(C=N) and ν(N-O) groups stretching vibrations, respectively. These absorptions are in good agreement with the values reported for similar compounds.[14,15,17,22]

In the IR spectrum of the complexes, the ν(O-H) bands due to water molecules were assigned at 3200-3600 cm^{-1}. These very broad bands prohibit the appearance of other bands in the region. Both complexes show weak and sharp ν(C=N) stretching bands centered in the 1617-1618 cm^{-1} range, corresponding to the ν(C=N) of the azomethine of imine.[14,15,17,22] In the IR spectra of ligands H_2L^1 and H_2L^2, the disappearance of this band is further evidence for tetrahydroquinazoline ring formation. After complexation, the appearance of the new ν(C=N) stretching band, the shift of the ν(N-O) bands to the upper frequency region, and the shift of the ν(C=N) of oxime bands to the lower frequency region in the IR spectrum of cobalt complexes may be attributed to N,N-chelation. These observations indicate the involvement of both the nitrogen atoms of the azomethine ν(C=N) of imine group and the azomethine ν(C=N) of oxime group to the coordination with the metal. In addition, the non-ligand bands at 458 cm^{-1} are tentatively assigned to υ(M-N) stretching vibrations.[23,33−35]

Table 2. Characteristic infrared bands (cm^{-1}) of the compounds (KBr pellets).

Compound	NH/NH_2	H_2O / O-H (O–H– – –N)	C=N		C=O	N-O	M-N
			oxime	imine			
2-ABA[31]	3379; 3399	–	–	–	–	–	–
INAP	–	3286 b	1650	–	1680	984 m, sh	–
INAP[32]	–	3282 s, b	1650 sh	–	1683 s	870 s	–
(H_2L^1)	3261 m, sh; 3399 m, sh	(2764) b	1606	–	–	947 s, sh	–
([$CoL^1(HL^1)$].H_2O)	–	3200-3600 b	1584 m	1617 w	–	964 w	458 w
INAT	–	3186 b	1543	–	1594	930	–
INAT[29]		3186[c]			1592[c]		
(H_2L^2)	3264 m, sh; 3393 m, sh	(2768) b	1606 m	–	–	937 s,sh	–
([$CoL^2(HL^2)$].H_2O)	–	3200-3600 b	1580	1618	–	941 w	458 w

w: weak, m: medium, s: strong, b: broad, sh: sharp, c: Nujol, intramolecular hydrogen bonding

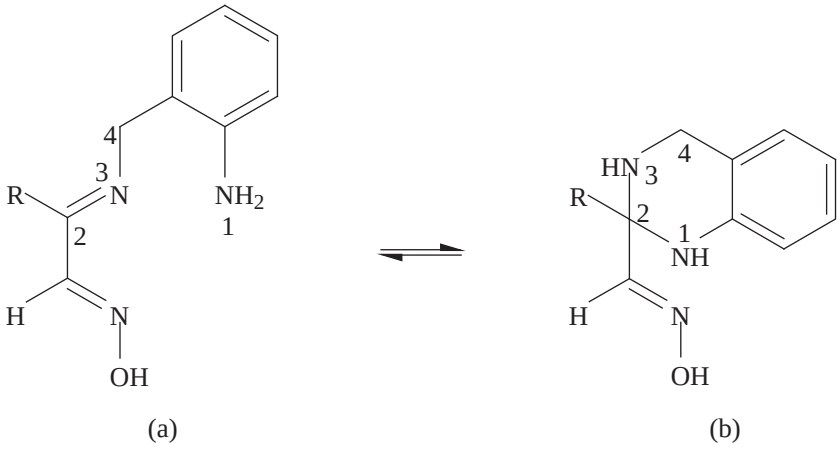

Figure 3. Ring form including numbering for tetrahydroquinazoline oxime derivative ligands. (a) Aniline type chain form (b) ring form.[8]

NMR analysis and structure determination

The ^{1}H-NMR spectra (400 MHz) of the α-carbonyl oximes, tetrahydroquinazoline oximes, and their corresponding cobalt(III) complexes recorded in deuterated dimethyl sulfoxide are presented in Tables 3 and 4. The ligands H_2L^1 and H_2L^2 show signals corresponding to the D_2O exchangeable –NOH (oxime, 1H), -NH (tetrahydroquinazoline ring nitrogen-1, 1H) and -NH (tetrahydroquinazoline ring nitrogen-3, 1H) protons at ca. δ 10.81-10.91 ppm (s), 6.64-6.71 ppm (s), and 2.99-3.29 ppm (for H_2L^1 br, for H_2L^2 m), respectively. For the HC=N proton, a singlet occurs in the 7.44-7.45 ppm region. The integration of the ^{1}H-NMR spectrum suggests the presence of a range of proton resonances between 6.45 and 7.57 ppm because of the resonance

of 9 phenyl protons of H_2L^1. Moreover, the ligand H_2L^2 shows signals corresponding to the resonance of 7 phenyl and thienyl protons at ca. δ 6.47-7.41 ppm.

Table 3. ^{1}H-NMR spectral data (δ, ppm) and coupling constants (Hz) of the 2-ABA, INAP, H_2L^1, and its cobalt(III) complex (in DMSO-D_6).

	2-ABA[(31)e]	INAP	H_2L^1	$[CoL^1(HL^1)].H_2O$
-CH_2	3.85	–	3.57 AB system, J = 17.0, 2H	4.82 m, 4H
OH[f]	–	12.68 s, 1H	10.81 s, 1H	–
NH_2	1.25 - 1.75; 4.15 - 4.80	–	–	7.43 - 7.49 2H
NH[f]	–	–	2.99 - 3.17 b, w, 1H; 6.60 s, sh, 1H	7.26 - 7.32 1H
Phenyl	6.65; 6.69; 7.02; 7.07, 4H	7.51 t, J = 7.8, 2H; 7.64 t, J = 7.4, 1H; 7.95 dd, J = 8.4, 1.2, 2H	6.45 td, J = 7.6, 1.2, 1H; 6.72 t, J = 7.0, 2H; 6.90 td, J = 7.2, 1.6, 1H; 7.23 t, J = 7.6, 1H; 7.31 t, J = 7.6, 2H; 7.57 d, J = 7.2, 2H	7.11 - 7.69 m, 18H
H-C=N	–	8.02 s, 1H	7.42 s, 1H	6.89 s, 2H

s: singlet, d: doublet, t: triplet, m: multiplet, b: broad, w: weak, sh: sharp, e: in $CDCl_3$, f: D_2O Exchange.

1,3-Unsubstituted tetrahydroquinazolines show chain-ring-chain tautomeric equilibria containing 1 cyclic form and 2 linear forms. The chain form is easy to differentiate from the ring form based on the proton and carbon signals of sp^2-hybridized C=N carbon and the proton attached to it.[8] In addition, the ring form can be easily identified from magnetically nonequivalent methylene protons (Figure 3).[8] Tetrahydroquinazoline derivative H_2L^1 has an AB system center at δ 3.57 ppm, J = 17.0 Hz. The other ligand H_2L^2 has a broad multiplet between 3.61 and 3.76 ppm. These signals are in good agreement with values reported for similar compounds[7,8,10] and are more evidence for tetrahydroquinazoline ring formation.

In the spectra of Co(III) complexes signals due to the –NOH group are absent and this is evidence for deprotonation of oxime groups. The chemical shift belonging to the –NH proton at position 3 in tetrahydroquinazoline oximes disappeared from the ^{1}H-NMR spectrum of cobalt complexes. Complexation in the integration of the ^{1}H-NMR spectrum of Co(III) complexes suggests the presence of a new range of proton resonances at ca. δ 7.26-7.46 and δ 7.43-7.77 ppm due to the resonance of one –NH and two –NH_2 protons of ligands. The downfield appearance and the D_2O exchangeable peaks were assigned by formation of the aniline type chain forms (Figure 3) and may be attributed to nitrogen atoms at position 1 of coordination.

In the cobalt complexes, the peaks due to the HC=N group showed a considerable upfield shift, and appeared at δ 6.89-7.14 ppm, which suggests that the nitrogen atom of the oxime group acts as a donor atom to the central metal ion, i.e. Co(III).[36] For the phenyl and thienyl protons, multiplets showed a downfield shift and appeared at δ 6.97-7.69 ppm.

Table 4. ^{1}H-NMR spectral data (δ, ppm) and coupling constants (Hz) of the 2-ABA, INAT, H_2L^2, and its cobalt(III) complex (in DMSO-D_6).

	2-ABA[31]e	INAT	H_2L^2	$[CoL^2(HL^2)].H_2O$
-CH_2	3.85	–	3.61 - 3.76 m, 2H	5.11 m, 4H
OH[f]	–	12.77 s, 1H	10.91 s, 1H	–
NH_2	1.25 - 1.75; 4.15 - 4.80	–	–	7.77 2H
NH[f]	–	–	3.24 -3.29 m, 1H; 6.71 s, 1H	7.46, 1H
Phenyl	6.65; 6.69; 7.02; 7.07, 4H	–	6.47 td, J = 7.2, 1.2, 1H; 6.68 dd, J = 8, 1,2, 1H; 6.75 d, J = 7.2, 1H; 6.89 dd, J = 7.4, 1.6, 1H	6.97 - 7.19 m, 8H
Thienyl	–	7.25 t, J= 5.0, 1H; 8.06 dd, J= 5.0, 1.0, 1H; 8.09 dd, J= 3.8, 1.0, 1H (7.00 - 7.18 m, 1H; 7.65 d, J= 5.4, 1H; 8.03 d, J= 3.6, 1H)[29]e	6.92 m 1H; 7.06 dd, J=3.4, 1.2, 1H; 7.41 dd, J=5.2, 1.2, 1H	7.31 - 7.38 m, 6H
H-C=N	–	7.97 s, 1H (7.89 s 1H)[29]e	7.45 s, 1H	7.14 s, 2H

s: singlet, d: doublet, t: triplet, m: multiplet, e: in $CDCl_3$, f: D_2O Exchange.

Furthermore, in the cobalt complexes, methylene protons' signals shift downfield. This situation confirms that aniline type linear forms are observed in complexes but methylene protons are different from the result obtained before.[8] After complexation, the appearance of these signals downfield verifies that nitrogen atoms of position 3 are coordinated to metals.

The ^{13}C-NMR spectra of the α-carbonyl oximes, tetrahydroquinazoline oximes, and their corresponding cobalt(III) complexes are presented in Tables 5 and 6. In the ^{13}C-NMR spectra of the α-carbonyl oxime derivatives INAP and INAT, the signal of the carbon atom of carbonyl group appears at 189.49-180.56 ppm but disappear in the ^{13}C-NMR spectra of the tetrahydroquinazoline oximes H_2L^1 and H_2L^2, which is evidence for the formation of new ligands. In the ^{13}C-NMR spectrum of tetrahydroquinazoline oxime derivatives (H_2L^1 and H_2L^2), the signals at 152.90-151.82 ppm and 42.34-42.08 ppm are attributed to the carbon atom of oxime group and carbon atom of methylene. In addition, the C=N carbon atom of α-iminooxime is not present in spectra and it is evidence that α-iminooxime is not formed. The ligands show signal corresponding to carbon atom of position 2 at ca. δ 71.25-69.59 ppm, which is evidence for tetrahydroquinazoline ring formation. These values are in good agreement with reported values.[7,8,10] All the signals in the 114.87-128.73 ppm and 125.93-127.10 ppm ranges are assigned to the carbon atoms of the phenyl and thienyl groups, respectively.

The chemical shift due to the carbon atom of position 2 in tetrahydroquinazoline oximes disappeared from the ^{13}C-NMR spectrum of cobalt complexes. After complexation a new resonance between 174.59 and 165.78 ppm was assigned by formation of the aniline type chain forms. In addition, the signals due to the

carbon atom of azomethine groups in α-iminooximes were shifted downfield in our work and this is evidence for nitrogen atoms at position 1 of coordination.

The chemical shifts belonging to the carbon atoms of oxime groups and methylene groups in the ligands H_2L^1 and H_2L^2 showed an upfield shift and a downfield shift on complexation with Co(III) and appeared at ca. δ 139.63-139.60 ppm and δ 53.60-53.71 ppm, respectively. These facts substantiate the conclusion obtained by the ^{1}H-NMR studies, i.e. the involvement of the oxime nitrogen and position of N-1 in coordination.

Table 5. ^{13}C-NMR spectral data (δ, ppm) of the 2-ABA, INAP, H_2L^1, and its cobalt(III) complex (in DMSO-D_6).

	2-ABA$^{(31)e}$	INAP	H_2L^1	$[CoL^1(HL^1)].H_2O$
$\underline{C}H_2$	44.95	–	42.34	53.60
Ph($\underline{C}$-H)	115.85-129.02	128.85-133.65	115.02-128.73	123.23-131.01
($\underline{C}$)-CH_2	126.19	–	120.72	128.38
Ph($\underline{C}$)-C$<^{N}_{N}$	–	–	143.99	–
Ph($\underline{C}$)-C=N	–	–	–	131.43
Ph($\underline{C}$)-C=O	–	136.54	–	–
Ph($\underline{C}$)-NH	–	–	143.69	139.12
Ph($\underline{C}$)-NH_2	146.29	–	–	–
$>\underline{C}<^{N}_{N}$	–	–	71.25	–
H-$\underline{C}$=N	–	148.18	152.90	139.63
Ph-$\underline{C}$=N	–	–	–	174.59
Ph-$\underline{C}$=O	–	189.49	–	–

e: in $CDCl_3$, Ph: phenyl

Table 6. ^{13}C-NMR spectral data (δ, ppm) of the 2-ABA, INAT, H_2L^2, and its cobalt(III) complex (in DMSO-D_6).

	2-ABA$^{(31)e}$	INAT	H_2L^2	$[CoL^2(HL^2)].H_2O$
$\underline{C}H_2$	44.95	–	42.08	53.71
Ph($\underline{C}$-H)	115.85-129.02	–	114.87-116.71	123.23-129.38
Th(C-H)	–	128.96-136.83	125.93-127.10	131.17-131.59
($\underline{C}$)-CH_2	126.19	–	120.31	128.45
Th($\underline{C}$)-C$<^{N}_{N}$	–	–	149.32	–
Th($\underline{C}$)-C=N	–	–	–	133.04
(Th($\underline{C}$)-C=O)	–	141.13	–	–
Ph($\underline{C}$)-NH	–	–	143.03	138.98
Ph($\underline{C}$)-NH_2	146.29	–	–	–
$>\underline{C}<^{N}_{N}$	–	–	69.59	–
H-$\underline{C}$=N	–	147.86	151.82	139.60
Th-$\underline{C}$=N	–	–	–	165.78
Th-$\underline{C}$=O	–	180.56	–	–

e: in $CDCl_3$, Ph: phenyl, Th: thienyl

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