The Novel bis-dioxime-based and Boronic acid-capped Groups Containing Fe(II) and Co(II) Complexes: Synthesis, Characterization and Spectroscopy

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Abstract: In the present work, firstly the novel monoxime **(1)** and asymmetric dioxime ligand **(LH_2) (2)** derived 4′-hydroxyvalerophenone as ketone was prepared under optimum reaction conditions. Then, the bis-dioxime-based and boronic acid-capped groups containing Fe(II) and Co(II) complexes **$[(L)_2M(X)_2(BA)_2]$ (3-6)** (L= Dioxime, M = Fe(II) or Co(II), X= Cl_2 or H_2O and BA = Butyl boronic acid (BBA) or Ferrocene boronic acid (FBA)) were synthesized into a two-necked round-bottom flask by direct interaction of the dioxime ligand **(2)**, and different boronic acid with metal salts ($FeCl_2.4H_2O$ or $CoCl_2$) without special requirement of any additional chemical process. The prepared ligands and their Fe(II) and Co(II) complexes were characterized by melting points, FT-IR, UV-Vis, LC-MS, NMR spectra (^1H and ^{13}C), elemental analysis, as well as magnetic susceptibility measurements. The spectroscopic results demonstrate that the proposed Fe(II) and Co(II) complexes consist of six-coordinated species and possess the octahedral geometry. The FT-IR spectra of the Fe(II) and Co(II) complexes reveal the existence of the characteristic peaks at range from 1208 to 1217 cm^{-1} corresponding to (B-O) stretching.

Keywords: Bis-dioximates, Fe(II) and Co(II) complexes, spectroscopy, boronic acid.

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INTRODUCTION

A comprehensive literature survey shows that the dioxime or *vic*-dioxime compounds are easy-to-handle, air-stable, distinctive structures and they have been considered as attractive raw materials for today's chemical industry and synthetic chemistry. Moreover, due to various electrochemical, spectroscopic, magnetic and catalytic properties of these compounds; different dioxime ligands and their metal complexes are of great importance in the study of molecular materials [1-4]. Besides these chemical properties, there were many reports in the literature dealing with the bis-dioxime-based and boronic acid-capped groups containing cage-type Fe(II) and Co(II) complexes for different purposes in modern chemistry. In recent years, the scope of *vic*-dioximes and their various metal complexes have been expanding among material scientists, pharmacists, chemists, biologists, physicists and so on due to their widespread potential applications.

Vic-dioximes ligands have three isomers which occur in *syn* (α), *anti* (β), and *amphi* (γ) arrangements, [5,6] respectively. The nomenclature of each isomer is defined by the location of the hydroxyl groups in corresponding dioxime compounds. In order to avoid locational limitations of the hydroxyl groups, different nomenclature techniques have been used for vic-dioximes. The metal complexes of anti isomers are more stable than the metal complexes formed by amphi isomers. The syn form of isomer does not form complex with metal ions due to the steric hindrance. The planar structure of 1,2-dioximes is balanced by hydrogen bonding interactions is also considered as the reason of the recognizable steadiness and sole electronic specifications of vic-dioxime complexes [7-10].

The literature research of the related bis-dioxime-based and boronic acid-capped groups containing vic-doxime complexes shows that the dioxime ligands widely used in synthesis studies, either a known ligand or the bought from commercial suppliers and used as received. Whereas, our research group has been synthesized dioxime ligands a straightforward and rapid two-step method from various ketones as newly compounds. In this context, the monoxime, dioxime ligand, and the bis-dioxime-based and boronic acid-capped groups containing Fe(II) and Co(II) complexes were synthesised. The synthesized compounds were characterized by UV-vis, FT-IR, LC-MS, ^{1}H and ^{13}C-NMR spectroscopic techniques, melting points, magnetic susceptibility measurements and elemental analysis.

EXPERIMENTAL SECTION

Materials and Measurements

Commercially available starting materials and organic solvents were purchased from their commercial sources and used as received. For dioxime ligands, the ^1H and ^{13}C NMR spectra were recorded on an Agilent-VNMRS-400 NMR operating at 400 and 100 MHz, respectively. The ^1H NMR chemical shifts were referenced to the residual solvent as determined relative to TMS (δ= 0 ppm) with chemical shifts given in parts per million at 25 °C. The NMR spectra of the Fe(II) and Co(II) complexes not measured because of the paramagnetic properties of complexes. Elemental analyses (C, H, and N) were performed on a LECO CHNS model 932 of the elemental analyser. FT-IR spectra were collected on a Perkin-Elmer Two UATR-FT spectrometer in the range of 400 to 4000 cm^{-1}. UV-visible spectra were obtained using quartz cells at 25 °C in a Perkin-Elmer model Lambda 25 spectrophotometer in the range of 200 to 1100 nm and C_2H_5OH/CH_2Cl_2 were used as solvents. The mass spectra (LC-MS) were obtained using an Agilent LC-MS/MS spectrometer. Magnetic susceptibilities data were performed on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants [11].

Synthesis of the monoxime (1) and the dioxime ligand (LH_2) (2)

In this study, the monoxime **(1)** and asymmetric dioxime ligand **(LH_2) (2)** are synthesized from 4′-hydroxyvalerophenone under optimum conditions, following the similar procedure with some modifications [12, 13]. The corresponding syntheses are briefly given in Scheme 1.

Monoxime (1): Color: pale yellow, yield: 82%, mp: 98 °C, Anal. Calc. for $C_{11}H_{13}NO_3$(%): C 63.75, H 6.32, N 6.76. Found: C 63.67, H 6.23, N 6.71. LC-MS (Scan ES^+): *m/z*: 207.2 (M^+, 15), 190.9 (25), 132.8 (45), 101.2 (100). IR (cm^{-1}): 3352 and 3222 υ(O-H), 3057 υ(Ar-CH), 2960-2861 υ(Aliph-CH), 1644 υ(C=O), 1605 υ(C=N), 1456-1426 υ(C=C), and 1224 υ(N-O). ^1H NMR (300 MHz, DMSO-d_6): δ: 10.56 (s, 1H, C=NO*H*), 7.42 (d, *J* 7.0 Hz, 2H, Ar-*H*), 6.82 (d, *J* 7.0 Hz, 2H, Ar-*H*), 3.59 (s, 1H, Ar-O*H*), 1.53-1.24 (m, 4H, CH_3-CH_2-CH_2), 2.11 (s, 3H, -CH_2-CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ: 185.60 (*C*=O), 154.82 (*C*=NOH), 131.7, 129.0, 127.5, 115.6 (Ar-*C*H), 28.6 (*C*H_2-CH_3), 26.7, 20.0 (*C*H_2-CH_2), 14.4 (CH_2-*C*H_3). UV (C_2H_3OH, *=shoulder peak) λmax: 284 nm, *293 nm; (CH_2Cl_2, *=shoulder peak)λ_{max}: 292 nm, *301 nm.

Dioxime ligand (LH_2) (2): Color: yellow, yield: 78%, mp: 123 °C, Anal. Calc. for $C_{11}H_{14}N_2O_3$(%): C 59.45, H 6.35, N 12.60. Found: C 59.38, H 6.28, N 12.51. LC-MS (Scan

ES^+): *m/z*: 223.00 (M+H, 12), 179.0 (75), 133.0 (35), 101.0 (100). IR (cm^{-1}): 3343 and 3219 υ(O-H), 3062 υ(Ar-CH), 2963-2866 υ(Aliph-CH), 1600 υ(C=N), 1511-1426 υ(C=C) and 1241 υ(N-O). ^{1}H NMR (300 MHz, DMSO-d_6,): δ: 10.78 (s, 1H, C=N-O*H*), 9.63 (br s, 1H, C=N-O*H*), 7.47 (d, *J* 7.2 Hz, 2H, Ar-C*H*), 6.78 (d, *J* 7.2 Hz, 2H, Ar-C*H*), 3.45 (s, 1H, Ar-O*H*), 1.58-1.29 (m, 4H, CH_3-CH_2-CH_2), 0.91 (t, *J* 3.0 Hz, 3H, -CH_2-CH_3). ^{13}C-NMR (75 MHz, DMSO-d_6,): δ: 158.4, 156.9 (*C*=NOH), 130.8, 128.8, 127.5, 115.6 (Ar-*C*H), 28.75 (*C*H_2-CH_3), 26.80, 22.83 (*C*H_2-CH_2), 14.31 (CH_2-*C*H_3). UV (C_2H_5OH, *=shoulder peak)λ_{max}: 224 nm, 262 nm, (CH_2Cl_2, *=shoulder peak)λmax: 223 nm, 257 nm, *329 nm.

General procedures for the synthesis of [$L_2MX_2(BA)_2$] (3-6) complexes

The Fe(II) and Co(II) complexes were synthesized using dioxime ligand **(2)**, and different boronic acid with metal salts ($FeCl_2.4H_2O$ or $CoCl_2$). In a 100 mL of two-necked round-bottom flask, a solution of dioxime ligand **(2)** (2.0 mol) in 60 mL of CH_3NO_2 was stirred at 25 °C under argon atmosphere for 15 min. to completely dissolve the dioxime ligand. Then, appropriate $FeCl_2.4H_2O$ or $CoCl_2$ salt (1.0 mol) was added to the reaction flask in small portions. Following to this step, butyl boronic acid (BBA) or ferrocene boronic acid (FBA) (2.0 mol) was added and the mixture was stirred under reflux for 8 h. After cooling to 25 °C , the solvent was evaporated to approximately half the original volume and the remaining solution was kept overnight, during which a dark orange or dark brown precipitate appeared. The precipitate was then collected, washed with diethyl ether, n-hexane, and cold ethanol and dried in vacuo. Finally, the corresponding metal complexes were recrystallized from CH_2Cl_2/n-hexane mixture.

[$(L)_2Fe(Cl)_2(BBA)_2$] (3): Color: brown, yield: 62%, mp: >300 °C, Anal. Calc. for $C_{30}H_{42}N_4O_6B_2FeCl_2$(%): C 51.25, H 6.02, N 7.97. Found: C 51.18, H 6.04, N 7.91. LC-MS (Scan ES^+): *m/z*: 703.3 (M^+, 25), 627.8 (35), 412.9 (55), 217.8 (100). μ_{eff}: 4.85 B.M. Λ_m: 12.6 ($\Omega^{-1}cm^2\ mol^{-1}$). IR ($cm^{-1}$): 3320 υ(O-H), 3059 υ(Ar-CH), 2957-2872 υ(Aliph-CH), 1649 υ(C=N), 1506-1412 υ(C=C), 1260 υ(N-O) and 1217 υ(B-O). UV (C_2H_5OH, *= shoulder peak) λmax: 221 nm, *274 nm, (CH_2Cl_2, *= shoulder peak) λ_{max}: 266 nm, 286 nm, 294 nm, *327 nm.

[$(L)_3Co(H_2O)_2(BBA)_2$] (4): Color: Dark brown, yield: 65%, mp: >300 °C, Anal. Calc. for $C_{30}H_{46}N_4O_8B_2Co$ (%): C 53.68, H 6.91, N 8.35. Found: C 53.63, H 6.88, N 8.28. LC-MS (Scan ES^+): *m/z*: 671.2 (M^+, 20), 369.2 (100), 309.1 (90), 240.2 (45). μ_{eff}: 3.86 B.M. Λ_m: 15.0 ($\Omega^{-1}cm^2\ mol^{-1}$). IR ($cm^{-1}$): 3324 υ(O-H), 3053 υ(Ar-CH), 2962-2869 υ(Aliph-CH), 1651 υ(C=N), 1509-1410 υ(C=C), 1266 υ(N-O) and 1219 υ(B-O). UV (C_2H_5OH *= shoulder peak) λmax: 226 nm, 256 nm, *404 nm, (CH_2Cl_2 *= shoulder peak) λmax: 269 nm, 285 nm, 297 nm, *386 nm.

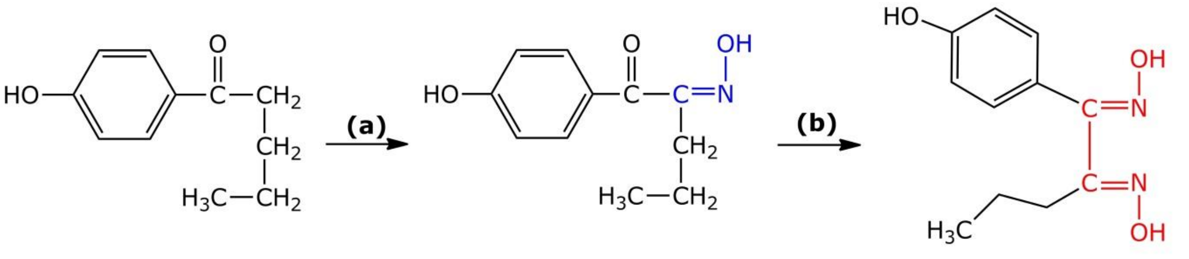
[(L)₂Fe(Cl)₂(FBA)₂] (5): Color: brown, yield: 69%, m.p: >300 °C, Anal. Calc. for $C_{42}H_{44}N_4O_6B_2Fe_3Cl_2$ (%): C 52.50, H 4.62, N 5.83. Found: C 52.46, H 4.58, N 5.80. LC-MS (Scan ES^+): *m/z*: 960.8 (M^+, 45), 765.5 (15), 526.7 (18), 146.7 (15). μ_{eff}: 4.94 B.M. Λ_m: 16.1 ($\Omega^{-1}cm^2$ mol^{-1}). IR (cm^{-1}): 3332 υ(O-H), 3064 υ(Ar-CH), 2954-2865 υ(Aliph-CH), 1652 υ(C=N), 1506-1432 υ(C=C), 1261 υ(N-O) and 1211 υ(B-O). UV (C_2H_5OH *= shoulder peak) λmax: 218 nm, 270 nm, *281 nm, 386 nm, (CH_2Cl_2 *= shoulder peak) λmax: 222 nm, 264 nm, *329 nm.

[(L)₂Co(H₂O)₂(FBA)₂] (6): Color: Dark brown, yield: 66%, m.p: >300 °C, Anal. Calc. for $C_{42}H_{48}N_4O_8B_2Fe_2Co$ (%): C 54.30, H 5.21, N 6.03. Found: C 54.28, H 5.23, N 6.29. LC-MS (Scan ES^+): *m/z*: 929.2 (M^+, 25), 572.3 (100), 463.0 (20), 218.3 (5). μ_{eff}: 3.84 B.M. Λ_m 18.4 ($\Omega^{-1}cm^2$ mol^{-1}). IR (cm^{-1}): 3326 υ(O-H), 3062 υ(Ar-CH), 2954-2872 υ(Aliph-CH), 1653 υ(C=N), 1509-1434 υ(C=C), 1260 υ(N-O) and 1208 υ(B-O). UV (C_2H_5OH *= shoulder peak) λmax: 220 nm, 271 nm, *368 nm, (CH_2Cl_2 *= shoulder peak) λmax: 225 nm, 260 nm, *324 nm, 374 nm.

RESULTS AND DISCUSSION

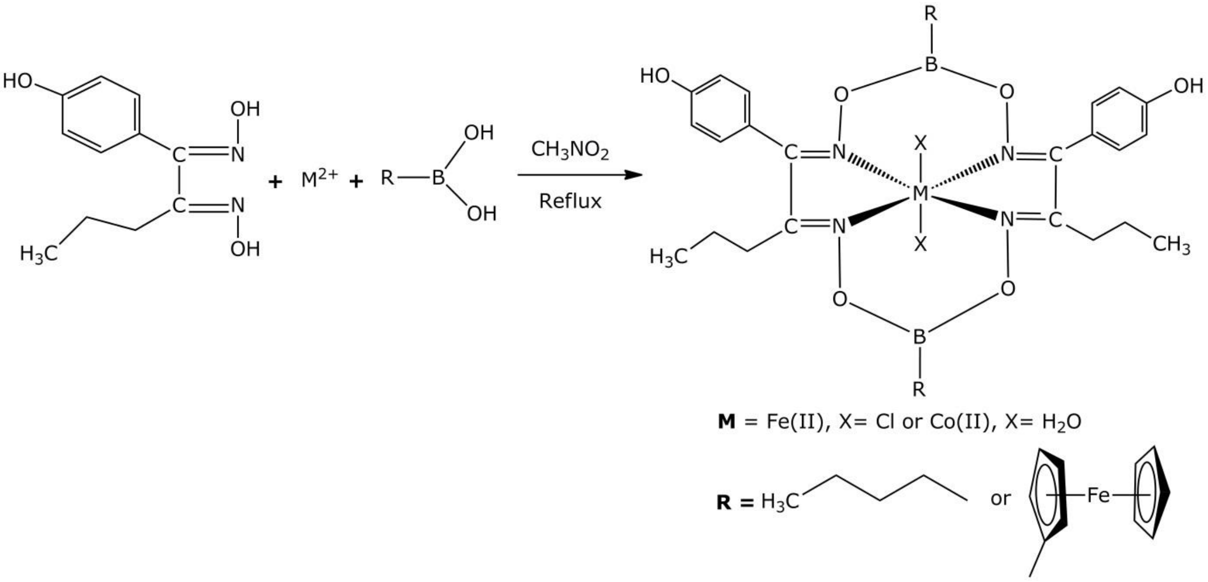
Synthesis

A summary of our synthetic route for ligands and their boron-capped Fe(II) and Co(II) complexes are given in Scheme 1 and 2, respectively. The synthesis of the monoxime **(1)** were carried out in the presence of C_2H_5ONa and n-butyl nitrite ($C_4H_9NO_2$) at -8 °C and gave the corresponding monoxime derivative, as pale-yellow solid, in moderate to good yield (82 %) (Scheme 1). After the characterization of monoxime **(1)**, the reaction of monoxime **(1)** with hydroxylamine hydrochloride ($NH_2OH.HCl$) in the presence of sodium acetate (CH_3COONa) and ethanol (as the solvent) were conducted under reflux. This synthetic procedure favoured the formation of the dioxime ligands as yellow crystals **(2)** (Scheme 1). The progress of the reactions were systematically monitored by Thin-Layer Chromatography (TLC). Then, the expected boron-capped Fe(II) and Co(II) complexes **(3-6)** have been synthesized via $FeCl_2.4H_2O$ or $CoCl_2$ salts and two equivalents of butyl boronic acid (BBA) or ferrocene boronic acid (FBA) with three equivalents of functionalized dioxime ligand **(2)** in CH_3NO_2 under reflux. Finally, we concluded that the synthesized ligands and their Fe(II) and Co(II) complexes optained the desired structures with enough purity for the spectroscopic methods, melting point, magnetic susceptibility measurements, and elemental analysis. The found and the calculated percentages of C, H and N results agree with each other, and these prove the proposed molecular formulas. All compounds are soluble in common organic solvents and stable at room temperature and normal pressure, and not sensitive to light.



4'-hydroxyvalerophenone **monoxime (1)** **dioxime ligand (LH_2) (2)**

Scheme 1. Synthesis of the proposed monoxime **(1)** and dioxime ligand (LH_2) **(2)**; **(a):** n-C_4H_9ONO/C_2H_5ONa, -5 °C, **(b):** $CH_3COONa/NH_2OH.HCl/EtOH$, reflux temperature.



Scheme 2. The structure of the proposed the boron-capped Fe(II) and Co(II) complexes **(3-6)**.

FT-IR Spectra

To have information about all compounds, FT-IR spectra of monoxime **(1)** and asymmetric dioxime ligand **(LH_2) (2)** with the boron-capped Fe(II) and Co(II) complexes **(3-6)** were evaluated in detail. In the FT-IR spectra of monoxime **(1)**, compared to the dioxime ligand **(2)**, the very strong stretching vibration of the (C=O) group at observed 1644 cm^{-1} is converted to the second (-C=N-OH) group after the formed dioxime ligand from monoxime **(1)**. However, when the FT-IR spectra of the dioxime ligand **(2)** were compared with that of the free monoxime **(1)**, a small frequency shift is exhibited which may be attributed to the formation of dioxime ligand (Figure S1). The FT-IR data on the proposed chemical structure of the boron-capped Fe(II) and Co(II) complexes **(3-6)** with asymmetric dioxime ligand **(2)** can be achieved by comparing to the FT-IR spectra of the free dioxime ligand with its Fe(II) and Co(II) complexes. The main spectral variations of the Fe(II) and Co(II) complexes, compared to the free dioxime ligand **(2)**, are found the presence of a new band at range 1208-1219 cm^{-1} have been assigned to the stretching vibrations of the (B-O) groups [14]. This idea is supported by the disappearance of the dioxime ligand υ(OH) peaks at around 3219 cm^{-1}, which provides clear evidence occurrence of the boron-capped Fe(II) and Co(II) complexes **(3-6)**. Another important observation for the boron-capped bis-dioximate Fe(II) and Co(II) complexes, the characteristic bands of the C=N, and N-O stretching vibrations have shifted almost between 53 cm^{-1} and 25 cm^{-1} to higher wave numbers upon coordination. This small shift exhibits the coordination of the dioxime ligands through their imine nitrogen atoms to the Fe(II) or Co(II) metal centers. Furthermore, the other stretching vibrations in the FT-IR spectra of all compounds support the formation of the desired compounds.

NMR Spectra

The ^{1}H and ^{13}C NMR spectra of the monoxime **(1)** and dioxime ligand **(2)** were recorded in DMSO-d_6 taking TMS as an internal standard. Further evidence for the formation of the monoxime **(1)** and dioxime ligand **(2)** were obtained from the ^{1}H and ^{13}C NMR spectra. The ^{1}H and ^{13}C NMR spectra of the monoxime **(1)** and dioxime ligand **(2)** were in good agreement with the target molecules. Detailed assignments of ^{1}H and ^{13}C NMR spectra along with coupling constants of the compounds have been presented in the experimental section. Due to the paramagnetic nature of the boron-capped bis-dioximate Fe(II) and Co(II) complexes, the NMR analysis could not be performed. The ^{1}H and ^{13}C-NMR spectra of dioxime ligand **(2)** depicted in Figure S2 and S3. It can be clearly seen that the appearance of the new proton and carbon signals assigned to the hydroxyl group of the oximes which is formed by the replacement of the carbonyl group by oxime moiety in monoxime **(1)**, as expected. This new deuterium-exchangeable proton and carbon peaks of the (C=N–O<u>*H*</u>) group of the dioxime ligands **(2)** are detected at 9.63 and 158.36 ppm in ^{1}H and ^{13}C-NMR spectra, respectively. Moreover, the absence of carbon peaks of the (C=O) group (185.60 ppm) in ^{13}C-NMR spectra for the dioxime ligands **(2)**, indicating the formation of the dioxime ligand from monoxime. Another relevant argument that confirms the formation is the presence of a new displayed peak at 3.59 ppm for monoxime **(1)** and at 3.45 ppm for the dioxime ligand **(2)** as singlet signals belonging to the ortho O<u>*H*</u> protons of a phenyl group, respectively. Furthermore, the other displayed proton and carbon peaks in the NMR spectra of the oxime ligands **(1)** and **(2)** also support the formation of the desired compounds.

UV-Vis Spectra

In order to obtain further structural information, the electronic spectra of the monoxime **(1)** and dioxime ligand **(2)** with their boron-capped Fe(II) and Co(II) complexes **(3-6)** have been measured. The electronic spectra of the monoxime **(1)** with dioxime ligand **(2)** and the boron-capped bis-dioximate Fe(II) and Co(II) complexes **(3-6)** were analyzed in C_2H_3OH and CH_2Cl_2 as solvents at room temperature, and the experimental techniques used to obtain the data is given in Figure S4 and Figure S5. In order to compare the UV-Vis spectra of the studied compounds, we have also investigated the electronic spectra of the Fe(II) and Co(II) complexes **(3-6)** along with that of dioxime ligand **(2)** under the similar experimental conditions. For the Fe(II) and Co(II) complexes, the characteristic spin-forbidden d-d transition of metal centers have not been observed in the visible region, most probably due to their very low molar absorption coefficient. However, when the UV-Vis results of the boron-capped bis-dioximate Fe(II) and Co(II) complexes were compared with that of the free dioxime **(2)** ligand, the ligand-to-metal charge transfer [LMCT, (L)→Fe(II) or Co(II)] or metal-to-ligand charge transfer [MLCT, Fe(II) or Co(II)→(L)] absorption bands was observed at range 368-404 nm, and these transitions which are clearly distincitve than other transitions might be attributed to the formation of metal complexes [14-16]. The capped boron groups and various metal centers might play a role in the spectral variations of ligand-to-metal charge transfer within the the Fe(II) and Co(II) complexes due to the same ligand in structures. Besides, The UV-Vis spectrum of the monoxime **(1)** and dioxime ligand **(2)** shows two or three absorption bands in the region 223-329 nm in C_2H_5OH or CH_2Cl_2 solvents, corresponding to the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions due to the (C=N–OH) oxime chromophore [17]. The reason of similarity in the shapes of UV-Vis absorption bands the dioxime ligand **(2)** and the boron-capped bis-dioximate Fe(II) and Co(II) complexes depends on the electron-withdrawing or electron-releasing group at different positions in the synthesised ligand and complexes. For Fe(II) and Co(II) complexes, these electronic spectra are observed at range 218-329 nm.

LC-MS Spectra

The LC-MS spectrum of the monoxime **(1)** and dioxime ligand **(2)** and their boron-capped bis-dioximate Fe(II) and Co(II) complexes **(3-6)** displays the principal fragment ions and the isotopic distributions of different intensities confirming their molecular weights (Figures S6-S10). The LC-MS spectra of the monoxime **(1)** and dioxime ligand **(2)** showed peaks attributed to the molecular ions m/z at 207.20 and 223.00, respectively. Whereas, the molecular ion peaks of the Fe(II) and Co(II) complexes **(3-6)** were displayed at m/z = 703.3 for $[(L)_2Fe(Cl)_2(BBA)_2]$ **(3)** complex, at m/z = 671.2 for $[(L)_2Co(H_2O)_2(BBA)_2]$ **(4)** complex, at m/z = 960.8 for $[(L)_2Fe(Cl)_2(FBA)_2]$ **(5)** complex, and at m/z = 929.2 for

$[(L)_2Co(H_2O)_2(FBA)_2]$ **(6)** complex, respectively. These mass spectra results are in good agreement with the calculated molecular weights of the target compounds.

Magnetic and Molar Conductivity Studies

The magnetic moments of the boron-capped bis-dioximate Fe(II) and Co(II) complexes **(3-6)** were measured at ambient temperature as B.M where $Hg[Co(SCN)_4]$ was used a calibrant. The metal complexes were found in paramagnetic character. The magnetic moment values for Fe(II) complexes found to be in the range of 4.85-4.96 B.M and this values is slightly different from the theoretical μ_{eff} =4.90 B.M for a high spin Fe^{2+} ion. The observed values in our case were very close to the high spin-only values for four unpaired electrons, and confirm the iron in +2 oxidation state with d^6 configuration and also octahedral geometry with sp^3d^2 hybridization. The magnetic moment values of Co(II) complexes found to be in range of 3.84-4.86 B.M and this values is slightly different from theoretical μ_{eff} =3.87 B.M for a high spin Co^{2+} ion which very close to the spin-only values for three unpaired electron, and confirm the cobalt in +2 oxidation state with d^7 configuration and also octahedral geometry and sp^3d^2 hybridization.

The molar conductivity values of the cage-type Fe(II) and Co(II) complexes **(3-6)** have been calculated in DMF at room temperature and are found in the range 12.6-18.4 Ω^{-1} cm^2 mol^{-1} which shows the non-electrolytic nature of the metal complexes.

CONCLUSIONS

Firstly, we have reported here the synthesis of the monoxime **(1)** and dioxime ligand **(2)** from 4′-hydroxyvalerophenone as ketone under ambient conditions. Then, from the reactions between $FeCl_2.4H_2O$ or $CoCl_2$ and dioxime ligand **(2)** in the mixture of CH_3NO_2 and various boronic acid, four Fe(II) and Co(II) complexes were obtained. The NMR spectra (^1H and ^{13}C for monoxime (1) and dioxime ligand (2)), FT-IR spectra, UV-Vis spectra, LC-MS, elemental analysis, melting point, and magnetic susceptibility measurements were used for characterization of ligand and their boron-capped Fe(II) and Co(II) complexes. The spectroscopic results showed that the Fe(II) and Co(II) complexes have six-coordinated species and octahedral geometry.

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