Physicochemical and Analytical Studies of Some Monomer and Polymer Complexes Derived from Selected Aroyl Hydrazone

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Abstract

New solid complexes derived from the reaction of aroyl hydrazones, 2-hydroxy-1-naphthaldehyde benzene sulphonyl hydrazone (HNB), and 2-hydroxy-1-naphthaldehyde p-toluene sulphonyl hydrazone (HNT), with Co2+, Ni2+, and Cu2+ salts have been isolated and characterized using elemental analyses, spectral (UV-vis., IR), molar conductivity and magnetic measurements. The modes of bonding as well as the stereochemistry of the isolated solid complexes were discussed. The results suggested that both HNB and HNT coor-dinated with the metal ions in a bidentate manner forming a polymeric chain in the case of HNB while monocular complexes were formed in the case of HNT. The amounts of solvent in the solid complexes were determined by TGA measurements. Also, spectral studies of HNT with Co2+ and Fe3+ ions in solution were carried and the ratio of complexes was determined by continuous variation, molar ratio, and slope ratio methods. Moreover, the results suggest the formation of 1:1 (M:L) for Co2+ ions while three species with ratios of 1:1, 1:2, and 2:1 (M:L) have been observed in the case of Ni2+ and Cu2+. Finally, conductance titration of HNB and HNT with Co2+ ion elucidates the formation of two species with ratios 1:1 and 1:2 (M:L) in the case of the Co2+-HNB while 1:1 (M:L) belongs to the Co2+-HNT system.

Keywords

Aroyl Hydrazones Complexes, Polymer and Monomer Complexes, FTIR, Synthesis, Stoichiometry of Complexes

1. Introduction

It is well known that hydrazones occupied a central role in the development of
coordination chemistry. This feature comes from the fact that the hydrazones, derived from the condensation of α-hydroxyl or methoxy aldehydes and ketones with hydrazides, are potential polynucleating ligands possessing azomethine and phenol or methoxy functions [1] offering varying bonding possibilities in metal complexes. Studies of some metal chelates of hydrazones derivatives are well known in literature [2]-[10].

On introducing the SO₂ group instead of the carbonyl group (CO) of the hydrazones moiety, the compounds are called sulphonyl hydrazones having the following formula, RSO₂NHN=CHR'. Bivalent metal complexes of benzene sulphonyl hydrazide (BS) have been studied [11]. It was reported earlier that BS coordinates to the central metal ion through the SO₂ and nitrogen of the NH group with the removal of NH proton where a polymeric chain has been suggested [12]. Moreover, salicylidene benzene sulphonyl hydrazone (HSBS) with some transition metals (M = Co²⁺, Ni²⁺, Cu²⁺, Hg²⁺, Zn²⁺, and Cd²⁺) was synthesized and characterized by different physicochemical techniques. The results showed that Ni²⁺, Cu²⁺, and Hg²⁺ form complexes with the general formula, [M(SBS)₂], while Co²⁺, Zn²⁺, and Cd²⁺ form complexes with the polymeric formula [M(SBS)₂]ₙ. The ligand acted in the latter case in a bidentate fashion via the NH and SO₂ groups (with deprotonation of the NH group forming a polymeric structure [12].

Finally, Cu²⁺ and Ni²⁺ complexes of hydrazones derived from benzene sulphonyl hydrazine with salicylaldehyde and 2-hydroxy-1-naphthaldehyde were studied by physical and spectral methods [13]. Based on elemental analyses and spectral (i.r. and n.m.r.) data the results suggest that the isolated hydrazones behave as monobasic bidentate towards the metal cations and coordinate through the C=N and deprotonated phenol OH groups. It is worth mentioning ion that the spectral (Uv-vis.), magnetism as well as thermal (TG, DTG, and DTA) measurements were not been investigated for these complexes. In addition, some data obtained in this work differs from that reported before [13].

The goal of this paper is to synthesize and characterize the stereochemistry of the solid complexes derived from the reaction of 2-hydroxy-1-naphthaldehyde-benzene-sulphonylhydrazone (HNB), p-toluene-(HNT) with Co²⁺, Ni²⁺ and, Cu²⁺ salts. The effect of the methyl group that represents the only difference between the two synthesized hydrazones on their coordinating nature has been illustrated. Furthermore, the pKₐ values of HNB and HNT were determined and the stoichiometry of complexes in solution has been determined by spectrophotometric and conductance techniques.

2. Experimental

All chemicals and solvents utilized were of BDH or AR quality and used without further purification. ¹H-NMR spectra in d₆-DMSO with TMS as internal standard were obtained from a Jeol-FX-90Q Fourier NMR spectrometer at Cairo University, Egypt. IR spectra were recorded as KBr pellet in the range 200-4000
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cm⁻¹ on a Mattson 5000 FTIR spectrometer at Mansoura University. Mass spectra of the ligands were performed by a Shimadzu-GC-MS-QP1000 EX using the direct inlet system at Cairo University, Egypt. Elemental analyses were determined using Perkin-Elmer 2400 at Cairo University, Egypt (Table 1). Metal contents were estimated using EDTA as reported earlier [14] [15] [16]. UV-vis. spectra of the samples in Nujol mull or DMSO, and in DMSO were measured in the range of 200 - 1000 nm using a Unicam UV2-100 spectrophotometer at Mansoura University, Egypt. The mass susceptibility of the solid complexes (χₐ) was measured with a magnetic susceptibility balance of model Sherwood at Mansoura University, Egypt. The thermal analyses (TG, DTG, and DTA) under nitrogen were carried out with a Shimadzu 50 H thermal analyzer at Mansoura University, Egypt.

2.1. Preparation of Benzene Sulphonyl Hydrazine (BH)

Benzene sulphonyl hydrazine (BH) was prepared as described earlier in the literature [11]. The isolated product was crystallized from bi-distilled water and dried in the air. A yellowish-white crystal was obtained (Mp. = 94°C).

2.2. Preparation of Hydrazones Ligands (HNB, HNT)

The two ligands, HNB and HNT, were synthesized by adding BH (0.02 mol, 3.44 g) dissolved in absolute methanol (50 mL) to a solution (50 mL) of 2-hydroxy-1-naphthaldehyde (0.02 mol, 3.44 g) (HNB) and 2-hydroxy-1-naphthaldehyde p-toluene sulphonyl hydrazone (HNT), respectively. The reaction mixtures were refluxed for 3 h in a water bath (95°C). The product is separated out by concentrating the solution to half of its volume and cooling. The crystals of the desired ligand were filtered off and finally recrystallized from methanol. The chemical structures of the resulting hydrazones are shown in Figure 1.

2.3. Preparation of Solid Complexes

All the isolated solid complexes (Table 1) were prepared by mixing equivocal amounts of ligands and M(II) acetates (M = Co²⁺, Ni²⁺, and Cu²⁺) in 100 mL ethanol. The reaction mixture was refluxed in a water bath (95°C) for 6 h. The colored microcrystalline solids were isolated by filtration on hot, washed repeatedly

**Figure 1.** Chemical structures of hydrazones.
with hot ethanol, and ether, and finally dried in an oven at 80°C for 24 h.

2.4. Preparation of Solutions for Spectrophotometric Measurements

The appropriate concentration of the metal ions (Co²⁺ and Fe³⁺) and ligands were mixed in an absolute methanol solution. The final volume of the mixture was always kept constant by adding absolute methanol. All the absorbance measurements were recorded in the range “200 - 800 nm”. Methanol was used as a blank in the case of Fe³⁺ complexes while the ligand was used as a blank in the case of Co²⁺ complexes.

3. Results and Discussion

All the analytical, physical, and spectroscopic data of the hydrazones and their isolated metal complexes are recorded in Table 1 & Table 2. A comparison of the analyses for both the calculated and found percentages indicates that the composition of the isolated solid complexes coincides with the proposed formulae. All trials to isolate mono- or tris-ligand chelates by direct reaction of the ligands with the M(II) salts were unsuccessful. The complexes are air-stable for a long time, insoluble in water, alcohols, and carbon tetrachloride, and soluble in DMF and DMSO.

Table 1. Analytical, physical and spectroscopic data of the hydrazones and their complexes.

| Compound | M.p. (°C), Color | Found (Calcd.)% | δ-H-NMR Chemical shift (δ ppm)** | µeff | M⁺ | Λ⁺ | pKₐ | y |
|-----------|------------------|-----------------|---------------------------------|-----|-----|-----|-----|---|
| HNB, L₁ C₁₂H₁₄N₂O₅S | 154 Yellowish brown | 63.3 (62.6) | 11.6 (NH, s), 11.2 (OH, s)⁹, 8.85 (CH=N, s), 326 | 326.4 | 6.5 |
| [Cu(L₁)]₂-nH₂O | 206 Yellowish brown | 55.9 (55.8) | 8.2 (8.7) | 1.82 | - | 8.1 |
| [Ni(L₁)₂.(EtOH)½]n∙2nH₂O | >300 Pale green | 58.3 (57.4) | 7.9 (8.0) | Diamag. | - | 15.0 |
| [Co(L₁)]n | >300 Brick red | 57.5 (57.4) | 8.3 (8.0) | 2.34 | - | 18 |
| HNT, L₂ C₁₃H₁₆N₂O₅S | 172 Yellowish white | 64 (63.5) | 9.8 (NH, s), 9.4 (OH, s)⁹, 7.0 (CH=N, s), 1.4 (CH₃, s), 5 - 7 (naphthyl and phenyl rings, m) | 340 | 340.4 | 9.5 |
| [Cu(L₂)]∙1/2EtOH | 222 Yellowish brown | 59 (58.1) | 7.9 (8.3) | 2.06 | - | 13 |
| [Ni(L₂)₂.(EtOH)½] | 291 Pale green | 59.1 (58.4) | 7.3 (7.7) | Diamag. | - | 11 |
| [Co(L₂)]∙1/2EtOH-1/2H₂O | 249 Brown | 57.6 (57.7) | 8.0 (7.7) | 2.5 | - | 18 |
The positions of the IR bands of hydrazones and their metal complexes are summarized in Table 2. The IR spectra of HNB and HNT showed a strong band at 1620 - 1624 cm⁻¹ assigned to ν(C=N) of the azomethine. The observation of this band emphasizes the formation of the azomethine linkage. Each ligand also has a strong band in the region of 700 - 800 cm⁻¹ corresponding to the out-of-plane deformation of the aromatic rings. The observation of broad but weak bands in the 2000 - 1700 cm⁻¹ region for HNB and HNT is taken as evidence for the formation of a stable six-membered ring of intermolecular hydrogen bond of the type OH…N [17].

The IR spectral data for Co²⁺, Ni²⁺ and Cu²⁺-HNB complexes pointed out that HNB behaves as a bidentate ligand coordinating to one metal ion via the SO₂ and OH groups with a displacement of a proton from the latter group tending to form a polymeric chain structure (Figure 2). A worthy mention, it was reported that the Co²⁺ ion forms a polymeric chain with salicyldene benzene sulphony-hydrazone [12]. In fact, this suggestion is assumed on the basis of the following pieces of evidence (Table 2): 1) The characteristic main band of the SO₂ group at

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**Table 2.** IR and electronic absorption data of hydrazones and their complexes.

| Compound | ν (OH) | ν (NH) | νas (SO₂) | νs (SO₂) | δ (SO₂) | δ (OH) | ν (C=O) | ν M-O/ M-N | λmax, nm | Structure |
|----------|--------|--------|-----------|----------|---------|--------|---------|-------------|----------|-----------|
| HNB, L₁ C₁₀H₁₂N₂O₃S | 3450 | 3161 | 1620 | 1318 | 1167 | 574 | 1241 | 1077 | 366 (n-π*, SO₂), 354 (n-π*, C=O), 320 (π → π*), 254 (π → π*, naphthyl) | pesudo-tetrahedral |
| [Cu(L₁)₂]∙nH₂O | - | 3217 | 1615 | 1332 | 1170 | 576 | - | 1089 | 3300 - 3600 | 713 (B₂ → Ω), 417 (CT) |
| [Ni(L₁)₂(EtOH)₁/₂]∙nH₂O | - | 3204 | 1617 | 1329 | 1170 | 582 | - | 1089 | 3300 - 3600 | 620 (A¹ → E//), 466 (A¹ → E//) |
| [Co(L₁)]₂ | - | 3205 | 1616 | 1328 | 1165 | 585 | - | 1090 | 535/385 |
| HNT, L₂ C₁₀H₁₀N₂O₃S | 3470 | 3196 | 1624 | 1328 | 1164 | 572 | 1275 | 1075 | 474 (n-π*, SO₂), 442 (n-π*, C=O), 390 (π → π*, SO₂), 366 (π → π*, naphthyl), 336 (π → π*, phenyl) |
| [Cu(L₂)]∙1/₂EtOH | - | 3219 | 1600 | 1330 | 1168 | 574 | - | 1090 | 3300 - 3600 | 716 (B₂ → Ω), 402 (CT) |
| [Ni(L₂)₂(EtOH)₁/₂] | - | 3207 | 1600 | 1325 | 1168 | 579 | - | 1090 | 3300 - 3600 | 610 (A¹ → E//), 478 (A¹ → E//) |
| [Co(L₂)]∙1/₂EtOH∙1/₂H₂O | - | 3208 | 1597 | 1322 | 1167 | 581 | - | 1089 | 3300 - 3600 | 535 (A₁g → B₁g) |

Δis disappeared on adding D₂O, †(Co-HNT system, λmax = 385 nm), ‡(Fe-HNT system, λmax = 530 nm), §(Fe-HNT system, λmax = 670 nm).

### 3.1. IR Spectra

The positions of the IR bands of hydrazones and their metal complexes are summarized in Table 2. The IR spectra of HNB and HNT showed a strong band at 1620 - 1624 cm⁻¹ assigned to ν(C=N) of the azomethine. The observation of this band emphasizes the formation of the azomethine linkage. Each ligand also has a strong band in the region of 700 - 800 cm⁻¹ corresponding to the out-of-plane deformation of the aromatic rings. The observation of broad but weak bands in the 2000 - 1700 cm⁻¹ region for HNB and HNT is taken as evidence for the formation of a stable six-membered ring of intermolecular hydrogen bond of the type OH…N [17].

The IR spectral data for Co²⁺, Ni²⁺ and Cu²⁺-HNB complexes pointed out that HNB behaves as a bidentate ligand coordinating to one metal ion via the SO₂ and OH groups with a displacement of a proton from the latter group tending to form a polymeric chain structure (Figure 2). A worthy mention, it was reported that the Co²⁺ ion forms a polymeric chain with salicyldene benzene sulphony-hydrazone [12]. In fact, this suggestion is assumed on the basis of the following pieces of evidence (Table 2): 1) The characteristic main band of the SO₂ group at

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1318 cm\(^{-1}\) assigned to \(\nu_{\text{as}}(\text{SO}_2)\) shifts to a higher wavenumber by 10 - 14 cm\(^{-1}\) indicating that this group is taking part in bonding, 2) the disappearance of both \(\nu(\text{OH})\) and \(\delta(\text{OH})\) bands elucidates the deprotonation of this group, 3) the positive shift of \(\nu(\text{C-O})\) band indicates the formation of (–C-O-M) bond. Nevertheless, C=N was expected to involve in coordination in the case of HNB complexes, it was excluded here due to the absence of any significant shift or variation in its position or intensity upon chelating. This result is not consistent with the previously published data [12] [13]. Meanwhile, HNT coordinates in a bidentate fashion to one metal ion via the azomethine nitrogen (C=N) and OH groups (Figure 3). Displacement of a hydrogen proton from the latter group leads to a
six-membered ring around the central metal ion. This behavior is proposed on
the basis of (Table 2): 1) the characteristic three main bands of the SO₂ group at
1318, 1167 and 574 cm⁻¹ remain more or less at the same positions excluding the
participation of this group in coordination, 2) the bands of both ν(OH) and
δ(OH) vibrations disappear, and the ν(C-O) band is shifting to a higher fre-
quency, 3) the negative shift of the azomethine group to lower wavenumber con-
firms the involvement of this group in bonding [18]. In spite of this group is
not taking part in coordination in the case of HNB which is nearly resembled in
its chemical structure to HNT, it is involved here. This can be interpreted on the
basis of the presence of an electron-donating group (methyl) in the para position
for -SO₂NHN=C. This group increases the electron density on the azomethine
nitrogen (N=C) of HNT (in comparison to HNB) and subsequently, its donating
nature increases facilitating its linking to the metal.

Indeed, the appearance of ν(NH) band with its shift to higher wavenumber in
all synthesized complexes may be due to the destruction of the intermolecular
hydrogen bonding between the OH and C=N groups or presumably due to the
rupture of an intermolecular hydrogen bond of the type N-H…..N-H suggesting
of this intermolecular H-bonding arises from the observation of δ(NH) in the
¹H-NMR spectra of HNB and HNT at a higher position compared with that re-
ported in the literature. Moreover, the persistence of new bands in the IR spectra
of metal complexes as shown in Table 2 assigned to M-O and/or M-N indicates
the formation of the metal complexes. The observation of only one band for each
Co-N and Co-O group suggests the existence of trans-configuration [19]. Strong
broad absorption in the 3300 - 3600 cm⁻¹ region for metal complexes substan-
tiates the presence of water and/or ethanol.

3.2. ¹H-NMR Spectra

The assignments of the main signals in ¹H-NMR spectra of the ligands under
investigation are shown in Table 1. ¹H-NMR spectra of hydrazones exhibit three
signals with equal integration (1:1:1) at (11.59, 11.2, 8.85) and (9.8, 9.4, 7.0) ppm,
downfield of TMS, and assigned to the protons of (NH, OH, CH=N) of HNB
and HNT, respectively. On adding two drops of D₂O, the NH and OH signals
disappeared while the signal of CH=N remained. The higher frequency of the
OH signal(s) compared with that reported in the literature is most probably due
to the intermolecular hydrogen bonding operating between the hydrogen atom
of the ortho-hydroxyl group and the azomethine nitrogen (OH…N-type) as
previously confirmed by the IR data. By comparing the ¹H-NMR spectra of HNB
(HL₁) with its relating Ni(II) complex namely, [Ni(L₁)₂(EtOH)½]∙2H₂O, it is evident that 1) no signal is recorded for a phenol hydroxyl proton at 11.2 ppm,
as in case of the HNB hydrazones indicating deprotonation of the ortho-hydroxy
group 2) the remaining of the signals attributed to the proton of NH and CH=N
groups at nearly the same positions (Table 1) confirms the un participation of
these groups in coordination and thus coincides with the obtained IR data and
the proposed polymeric chain structure [20]. Perhaps, this comparison explains the coordination behavior of HNB with Co$^{2+}$ and Cu$^{2+}$ salts which are analogous complexes. It is well known that Co$^{2+}$, Ni$^{2+}$, and Cu$^{2+}$ ions are resembled in their chemical behavior due to the convergence in their ionic radii.

3.3. Electronic and Magnetic Spectra

The electronic spectra of the hydrazones and their solid metal complexes [21] [22] [23] [24] as well as the geometry and magnetic data of the formed chelates are shown in Table 2. The redshift of HNT bands in comparison to that observed in the case of HNB (Table 2) is mainly due to the existence of the methyl group in the para-position. This electron-donating group increases the electron density on the O=S=O, C=N, and OH groups, and consequently, a redshift was observed. The electronic spectra of the metal chelate suggest different environments around the metal ions. The results revealed that Cu$^{2+}$ complexes are pseudo-tetrahedral; Ni$^{II}$ complexes are trigonal-bipyramidal while Co$^{2+}$ complexes have square-planar geometry. For the magnetic studies, the values of $\mu_{\text{eff}}$ of all complexes may be considered in good agreement with the proposed structures [25] [26] [27].

3.4. Thermal Analysis

The thermal decomposition studies (TG, DTG, and/or DTA) on major solid metal complexes have been carried out. The TG curves up to 800˚C for complexes showed 3-5 stages of decompositions with the formation of metal carbonates/oxides/carbide or mixtures of them at the last stage. The results of the thermal analysis revealed that: 1) [Co(L$_1$)$_2$]$_n$ showed a first weight-loss stage at 219˚C assignable to the decomposition of the complex and at the same time emphasized the absence of any crystalline solvent. This temperature (219˚C) is high enough to be considered for out sphere ethanol or water. The TG curve is ended by the existence of CoCO$_3$, 2) [Co(L$_2$)$_2$.1/2EtOH.1/2H$_2$O decomposed at 275˚C and ended by CoCO$_3$ as well. The two weak bands in the range 100˚C - 200˚C suggest the removal of the solvent (1/2EtOH + 1/2H$_2$O), 3) [Ni(L$_1$)$_2$(EtOH)$_{1/2}$]$_n$.2nH$_2$O and [Ni(L$_2$)$_2$(EtOH)$_{1/2}$] decomposed at 134 and 322˚C, respectively. The residue corresponds to the formation of nickel carbonate, oxide, and carbide. The first weight-loss stage at 74˚C in case of [Ni(L$_1$)$_2$(EtOH)$_{1/2}$]$_n$.2nH$_2$O corresponds to the removal of 1/2EtOH + 2H$_2$O while the DTA diagram for [Ni(L$_2$)$_2$(EtOH)$_{1/2}$] showed an endothermic peak at 90˚C corresponding to the removal of 1/2EtOH molecule from the complex, 4) TG curve of [Cu(L$_2$)$_2$.1/2EtOH showed a first decomposition stage at 216˚C. This stage is accompanied by an exothermic peak in the DTA curve indicating the starting of decomposition. On the other hand, the DTA showed an endothermic peak at 102˚C assignable to the removal of 1/2EtOH.

In the light of the foregoing results, the most reasonable structures of the M(II) chelates can be represented by Figure 2 and Figure 3, respectively.
The behavior of Co$^{2+}$ and Fe$^{3+}$ ions with HNT has been studied and the stoichiometry was determined. The other ligand under investigation (HNB) is not investigated since it precipitates a solid complex with Co$^{2+}$ and gives unspecified color with Ni$^{2+}$ and Cu$^{2+}$ ions (i.e., a mixed color of HNB and metal (II) ion without any reaction).

### 3.5. Spectral Studies in Solution

Comparing the spectra of the Co$^{2+}$, and Fe$^{3+}$-HNT complexes with HNT and the employed metal salt solutions (cobalt acetate and ferric chloride) at room temperature showed a new band at 385 nm with a shoulder at 400 nm for Co$^{2+}$-HNT and a band at 670 nm in case of Fe$^{3+}$-HNT. Increasing the concentration of the ligand (from $1 \times 10^{-4}$ to $1 \times 10^{-4}$ M for Co$^{2+}$-HNT and to $6 \times 10^{-4}$ M for Fe$^{3+}$-HNT) leads to a hyperchromic shift without changing the position of the band manifesting the formation and stabilization of the complex in solution. On leaving Fe$^{2+}$-HNT solution for 42 h, it was noticed that the color of the solution has been changed from green to brown accompanied by a hypsochromic shift for the absorption maxima from $\lambda_{\text{max}}$ at 670 nm (green solution) to 530 nm (brown solution). This indicates that the Fe$^{3+}$ complex formed at once is quite stable but attains maximum stability after 42 h. Besides, it suggests the increase of 10 Dq, and consequently, the geometry of the complex may be changed. From this view, the effect of temperature on a Fe$^{3+}$-HNT is of considerable interest to be studied. Increasing the temperature from 25 to 55˚C for the Fe$^{3+}$-HNT system reveals a hypsochromic shift for $\lambda_{\text{max}}$ from 670 to 560 nm (Figure 4). Doubtless, this indicates that the increase of temperature helps too much for reaching the stability of the formed complex.

To trace the complex formation and deduce the stoichiometry of the complexes in solution, continuous variation [28], the molar ratio [29], and slope ratio [30] methods were employed. For the Co$^{2+}$-HNT mixture, the results obtained (at $\lambda_{\text{max}} = 385$ nm) by continuous variation (Figure 5), molar ratio, and slope ratio indicated the formation of the complex with 1:1 (Co$^{3+}$: HNT). On the
other hand, the results of continuous variation, molar ratio, and slope ratio methods for Fe³⁺-HNT mixture at the $\lambda_{\text{max}} = 670$ and 530 nm at once and after 42 h are in good agreement with each other and manifested the existence of 1:2 (Fe³⁺:HNT) and 2:1 (Fe³⁺:HNT) complexes, respectively. The continuous variation diagram (Figure 6, and Figure 7) revealed also a 1:1 (Fe³⁺:HNT) species at 530 nm, and high intensity for 2:1 (Fe³⁺:HNT) compared with 1:1 and 1:2 (Fe³⁺:HNT) indicating the higher stability of the 2:1 M:L complex. Based on the obtained results, it is suggested that 1:2 (Fe³⁺:HNT) was reached to 2:1 (Fe³⁺:HNT) passing by 1:1 (Fe³⁺:HNT). Also, It is very conspicuous that the stability of the 2:1 (Fe³⁺:HNT) complex increases with time and temperature. A literature survey pointed out that the octahedral $\text{FeF}_3^-$ showed a band at 704 nm while the tetrahedral $\text{FeBr}_4^-$ showed a band at 588 nm [31]. According to this fact, the hypsochromic shift of $\lambda_{\text{max}}$ from 670 to 530 nm may be due to two probabilities (1) the geometry of the Fe³⁺-HNT complex was changed from octahedral to tetrahedral due to the steric effect of ligand or (2). The kind of ligands was varied
but with preservation of the geometry i.e., the electronic field strength of ligands increased.

Spectrophotometric studies on the complexation of Co\(^{2+}\) and Fe\(^{3+}\) with HNT were performed in order to show the possibility of applying the reaction for the micro-determination of those two metal ions. Both Co\(^{2+}\) and Fe\(^{3+}\) ions are only selected within the all investigated meal ions since they exhibit a change in color which can be detected in the visible region. For this purpose, absorbance measurements were carried out by adding the metal salt solution in varying concentrations to a constant concentration of HNT in absolute MeOH. On plotting the obtained absorbance values at the above selected wavelengths (385, 670, and 530 nm) against the corresponding concentration of the metal ions to verify Beer’s law, linear relations were obtained (calibration curve). At a higher concentration of M\(^{n+}\), a negative deviation was observed. The results suggested that Beer’s law is obeyed for 1) Co\(^{2+}\)-HNT system at \(\lambda_{\text{max}} = 385\) nm up to \(0.1 \times 10^{-3}\) M, 2) Fe\(^{3+}\)-HNT (at once and RT) at, \(\lambda_{\text{max}}\)'s = 530 and 670 nm up to \(0.5 \times 10^{-3}\) M and 3) Fe\(^{3+}\)-HNT (after 42 h) at, \(\lambda_{\text{max}}\)'s = 530 and 670 nm up to \(2 \times 10^{-3}\) M. The sensitivity y values (Table 1) were estimated by Sandall’s method [32] following the equations:

\[
y = n\left(\text{at.wt}\right)/\varepsilon
\]
\[\varepsilon = A/bc\]

where:

\(y\) = sensitivity (number of micrograms of an element present as the absorbing species in a column solution of 1 cm\(^2\) cross-section giving an absorbency of 0.001 at specified wavelength).

\(n\) = number of elements in a molecule of the compound.

\(\text{At.wt}\) = atomic weight of the element in gram.
ε = molar absorptivity.
A = maximum absorbance obeyed Beer’s law.
c = concentration corresponding to the absorbance A.
b = thickness of the utilized quartz cell (1 cm).

3.6. Effete of pH on the Absorption Spectra of HNT and HNB

Absorption spectra of HNT (1 × 10^{-4} M) and HNB (1.2 × 10^{-5} M) in universal buffer solutions were recorded in the range of 200 - 450 nm. The spectra exhibit one band in the pH range 8 - 12 at 353 and 243 nm for HNB and HNT, respectively. No absorbance was traced in the lower pHs (1 - 7) in the case of HNB owing to the participation that occurred. The relation between absorbance versus the pH was represented in Figure 8 and Figure 9 shows the S-shape curve. The pKₐ values were calculated from these curves and located in Table 1.

![Figure 8. Effect of universal buffer on HNB ligand.](image1)

![Figure 9. Effect of universal buffer on HNT ligand.](image2)
smaller pK_a value of HNB (6.5) compared with that of HNT (9.5) arises from the effect of the electron-donating nature of the (CH₃) group in HNT which increases the electron density on the OH (naphthyl) group and consequently, the pK_a was observed at high pH value. On the other hand, the existence of a withdrawing group (phenyl) in HNB decreases the electron density on the OH (naphthyl) group and hence the pK_a has a small value.

Utilizing absolute methanol solutions, conductance titration of 10 mL (2.5 × 10⁻⁴ M) cobalt acetate solution with HNB (2.5 × 10⁻³ M) and 25 mL of cobalt acetate solution (5 × 10⁻⁴ M) with HNT (5 × 10⁻³ M) were carried out and represented in Figure 10 and Figure 11, respectively. The results of the Co²⁺-HNB curve (Figure 10) showed two breaks at 1:1 and 1:2 (Co²⁺:HNB). This illustrates that the two complex species with different ratios are possibly formed.
in solution and hence we could obtain each of them by adding the appropriate amount of the ligand. Fe$^{3+}$-HNB curve (Figure 11) revealed only one break at 1:2 (Co$^{2+}$:HNT).

A common behavior of these curves is the continuous decrease of the reaction mixture conductance with increasing the number of hydrazones added. This suggests the formation of non-electrolytic species in solution, i.e., the reaction of HNB or HNT with Co$^{2+}$ acetate proceeds without the liberation of acetic acid. Conversely, Co$^{2+}$-HNB, HNT complexes were isolated as solids by deprotonation of ligand and thus the acetic acid was liberated. This can be interpreted on the basis of various reaction conditions. To explain this contrariety, we proposed that HNB or HNT reacts with cobalt acetate in solution and at room temperature forming an octahedral geometry around the Co$^{2+}$ ion. Upon refluxing the reaction mixture, the liberation of acetic acid is induced and finally, a non-electrolytic complex species having a square-planar geometry is obtained as in the solid-state. This mechanism can be shown in case of HNB ligand as follow:

$$\begin{align*}
\text{RT (25 °C)} & \\
\text{HNB + Co(OAc)$_2$} & \rightarrow \\
\text{reflux} & \rightarrow \\
[\text{Co(HNB)$_2$(OAc)$_2$}] & \rightarrow \\
\text{[Co(HNB-H)$_2$]$_n$ + 2AcOH} & \\
\end{align*}$$

The same mechanism is proposed for the Co$^{2+}$-HNT complex. Finally, the molar conductivity of all complexes is shown in Table 1. The values indicate a non-electrolytic nature in this solvent and are consistent with the other results.

### 4. Conclusion

The results obtained in this work verified that a number of aroyl hydrazones complexes, derived from 2-hydroxy-1-naphthaldehyde, have been successfully synthesized. The compositions and structures of these complexes have been established on the basis of different physicochemical techniques. The mode of binding of the aroyl hydrazones under investigation mainly depends on the substitute in the para-position of the phenyl ring. The persistence of the electron-donating group in the para-position of phenyl ring e.g., methyl group increases the electron density on azomethine nitrogen and consequently facilitates its coordination with the metal cation. This is very conspicuous in the solid complexes of aroyl hydrazones with cobalt, nickel, and copper ions. The chelating takes place with the replacement of phenol hydrogen along with the linking of an auxiliary group that is SO$_2$ in HNB and C=N in HNT forming complexes with a ratio of 1:2 (M: L) composition for HNB and polymer chains with HNT. Spectrophotometric and conductance titration studies can be used to identify the stoichiometry of the aroyl hydrazones with some metal cations and the former technique substantiates the possibility of micro determination of Co$^{2+}$ and Fe$^{3+}$ ions by the aroyl hydrazones.

### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.
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