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Novel Hydrazone Derivatives and Their Tetracoordinated Metal Complexes

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New aroylhydrazone derivatives and their Co(II), Ni(II) and Cu(II) complexes have been synthesized and characterized by means of elemental analyses, molar conductances and magnetic measurements as well as electronic spectra, IR spectra, ^{1}H NMR spectra, ^{13}C NMR spectra and LC mass spectra. Ni(II) complexes were found to have general compositions [ML], where L = 2,6-dipiperidino-4-(2-hydroxybenzylidene hydrazino)-1,3,5-s-triazine; 2,6-dipiperidino-4-(5-bromo-2-hydroxybenzylidene hydrazino)-1,3,5-s-triazine, while other complexes have composition [ML_2] (M = Co^{2+} or Cu^{2+}). The infrared spectra indicate the coordination of imino nitrogen and phenolic oxygen atoms. Tetracoordinated structures are proposed for the Co(II) Ni(II) and Cu(II) complexes on the basis of magnetic evidence and electronic spectra.

Key Words: Aroylhydrazone, Tetracoordinated complexes, Dipiperidine, Triazine, Hydrazine.

INTRODUCTION

Hydrazone derivatives and their metal complexes have been widely studied due to their biological activities[1,2]. Hydrazone derivatives containing different donor atoms can act as good chelating agents for transition metal ions[3]. Aroylhydrazones are characterized by a -NH-N=C- group which imparts antiparasitic[4], fungicidal-bactericidal[5] and anticancer[6] properties to them.

We recently introduced the different chemistry of piperidino and their derivatives[7]. Piperidino derivatives have been reported as diazo compounds[8], polymer-supported reagents[9] and pharmacological properties[10]. Transition metals play a important in biological systems such as: decarboxylation, transamination, electron transfer, *etc.*[11].

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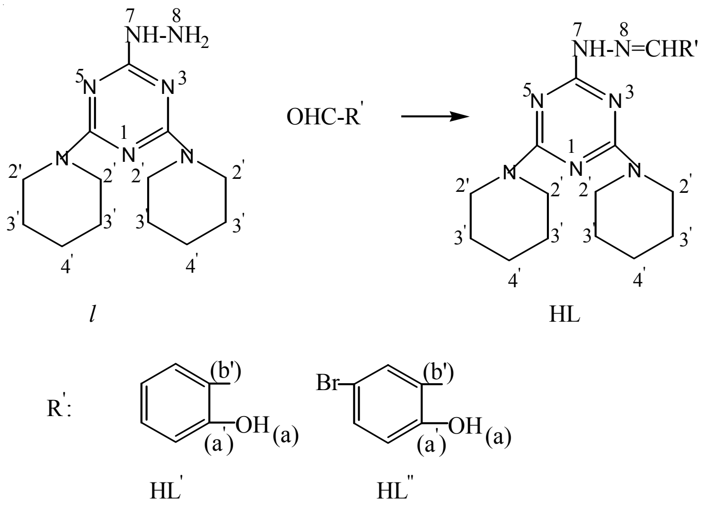
In order to contribute to these studies, we have prepared new hydrazone derivatives. To the best our knowledge, there are a few reports in the literature on synthesis of hydrazone derivatives using 4-hydrazino-1,3,5-s-triazine or 4-hydrazino-1,2,4-s-triazine[12]. However, hydrazone derivatives from 2,6-dipiperidino-4-hydrazino-1,3,5-s-triazine with reported aldehydes have not been synthesized yet. In order to prepare such a hydrazone derivative, we carried out with reaction between $NH_2NH_2 \cdot H_2O$ and 2,4,6-trichloro-1,3,5-s-triazine (Fig. 1).



HL′, 2,6-dipiperidino-4-(2-hydroxybenzylidenehydrazino)-1,3,5-s-triazine
HL″, 2,6-dipiperidino-4-(5-bromo-2-hydroxybenzylidenehydrazino)-1,3,5-s-triazine

Fig. 1. Structures of hydrazone derivatives

In this paper, we report synthesis and characterization of new hydrazones derived from 2,6-dipiperidino-4-hydrazino-1,3,5-s-triazine (L) with aldehydes and of their Co(II), Ni(II) and Cu(II) complexes.

EXPERIMENTAL

Synthesis of 2,6-dipiperidino-4-hydrazino-s-triazine (L):

First step: A solution of 2,4,6-trichloro-1,3,5-s-triazine (Ciyanüc Chlorür) (0.325 mol) in dioxane (50 mL) was added drop-wise to an dioxane solution (10 mL) of piperidine (0.065 mol) and then the solution was stirred for *ca.* 2 h. To this reaction solution was added drop-wise a solution (10 mL) of NaOH (2.6 g, 0.065 mol). The reaction mixture was stirred for 4 h on a water bath at 30-35 ºC. After cooling, the compound (A) separated was filtred and recrystallized from ethanol. The yield is 7.76 g (84.9 %); m.p. 117-119 ºC (Fig. 2).

Second step: To a solution of (A) (0.0276 mol) in ethanol (40 mL) the pertinent hydrazine (0.0823 mol) was added and then the solution was refluxed for *ca.* 4 h on a oil-bath. After cooling, the compound (L) was filtered off and recrystallized from ethanol[13]. The yield is 6.4 g (80.3 %). The compound was dissolved in MeOH, EtOH, THF, DMSO and DMF.

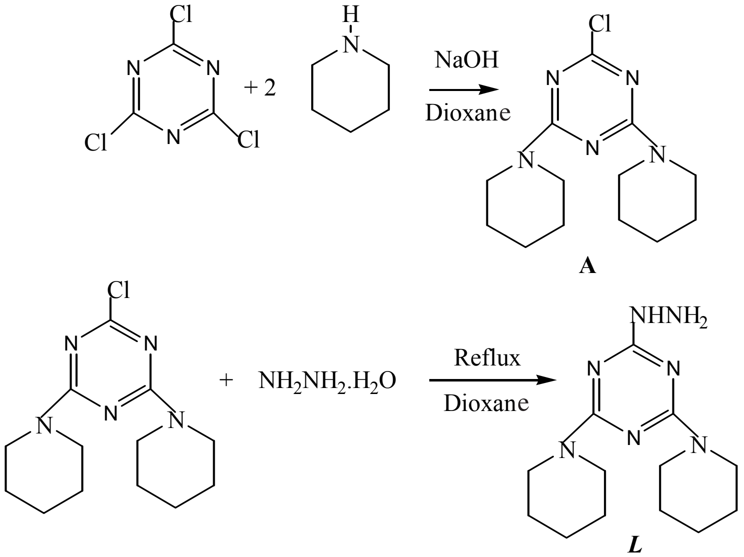


Fig. 2. Synthesis of 2,6-dipiperidino-4-hydrazino-s-triazine (L)

Sythesis of ligands: Two hydrazone derivatives were prepared by the following general procedure. To a solution of L in methanol (25 mL) respective aldehyde (1.25 mL) in methanol (25 mL) was added drop-wise with stirring. The resulting yellow solution was refluxed for 2 h. The reaction volumes were reduced to 10 mL by evaporation and then resulting yellow or deep-yellow precipitates were filtered and washed with diethyl ether. The compound was dissolved in THF, DMSO and DMF.

Synthesis of complexes: All the complexes are prepared by the following general method. A sample of $MCl_2 \cdot nH_2O$ (n: 6 for Co(II), Ni(II); n: 0 for Cu(II)) (0.30 g, 0.0013 mol) was dissolved in methanol (25 mL). To the solution of hydrazone derivatives (0.0013 mol) in methanol (25 mL) was added, immediately giving a green solution. The resulting solution was stirred for *ca.* 1 h, filtered and allowed to stand. On standing for a further 2 h, the solid complexes formed was collected by filtration, washed with a small volume of ethanol and dioxane and then, dried in a desiccator over $CaCl_2$.

All chemicals used in these investigation were reagent grade and were purified when necessary. All organic solvents used in these work were purified according to standard methods[14].

Elemental analyses were carried out with a LECO-CHNS-9320 instrument. Metal contents were determined by a Philips PU 9285 atomic absorption instrument. The analytical and physical data are listed in Table-1. ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX-400 MHz using TMS as an internal standard and dimethylsulfoxide (DMSO) as solvent. Mass spectra were recorded on a Micro Mass-UK Platform II mass spectrometer at Tubitak, Ankara, Turkey. Electronic spectra were recorded on an Unicam-UV2-100 spectrophotometer in DMF. IR spectra were recorded on a Mattson-5000 FT-IR instrument in KBr pellets. Melting points were determined with a Gallenkamp melting point apparatus. The molar conductivities were measured with a Siemens WPACM 35 conductivity meter (10^{-3} mol L^{-1} in DMF solution). Magnetic measurements were carried out with a Sherwood Scientific magnetic susceptibility balance (Model No: MK 1) at 21 ºC with $Hg[Co(NCS)_4]$ as a calibration.

RESULTS AND DISCUSSION

The reaction steps for the synthesis of aroylhyrazones are given in Fig. 2. The first step is the synthesis of 2,6-dipiperidino-4-chloro-1,3,5-s-triazine (A) from reaction of piperidine and 2,4,6-trichloro-1,3,5-s-triazine. In the second step, (A) and hydrazine monohydrate were reacted to obtain 2,6-dipiperidino-4-hydrazino-1,3,5-s-trizine (L). L was characterized by IR, ^1H- and ^{13}C NMR spectra. After that, L and two aldehydes were reacted to obtain new hydrazone derivatives (HL′ and HL″).

These hydrazone derivatives reacted with transition metal salts to give the corresponding complexes.

$$MCl_2\cdot nH_2O \;+\; L \xrightarrow[2\ h,\ 30\ ^{\circ}C]{\text{methanol}} [ML] \text{ or } [ML_2]$$

The aroyl hydrazone derivatives and their complexes are soluble in DMF and DMSO, but insoluble in other common organic solvents. Molar conductivities of their complexes are in the 2.3-6.7 Ω^{-1} cm^2 mol^{-1} range and commensurate with non-electrolytic behaviour[15].

Analytical, physical electronic and characteristic IR spectral data of the Schiff bases and complexes are given in Tables 1 and 2, respectively.

IR spectra of L, hydrazone derivatives and their complexes are summarized in Table-2. IR spectra of all hydrazone derivatives do not display any ν(R'-NH-CH=) bands at *ca.* 3100 cm^{-1} but exhibit ν(OH) bands at *ca.* 3400 cm^{-1}, indicating that in a solid state they remain as enols (Fig. 3a)[16]. Two strong bands at 3412 and 3325 cm^{-1} may be attributed to $-NH_2$ and -NH stretching vibrations for L, respectively (Fig. 1). Bands in the region of 3442-3386 and 3276-3071 cm^{-1} may be due to ν(OH) and ν(NH) modes, respectively. The former stretching vibrations are observed in HL′ and HL″,

TABLE-1
ANALYTICAL AND PHYSICAL DATA FOR HYDRAZON DERIVATIVES AND THEIR COMPLEXES

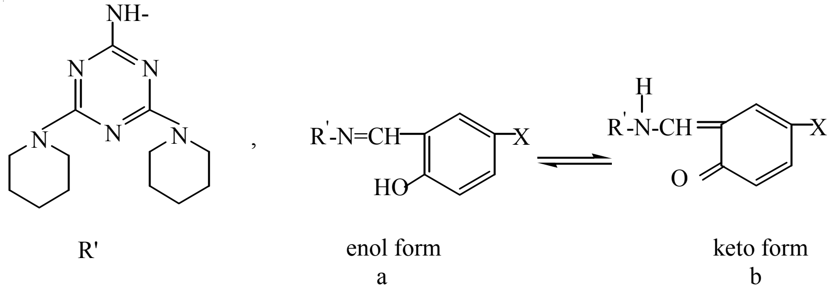
Compd.	m.f. (m.w.)	Colour Yield (%)	m.p. (ºC) μ_B	Elemental analysis (%): Found (Calcd.)			
				C	H	N	M
L	$C_{13}H_{23}N_7$ (277)	White 80	135.0 ± 0.8 -	56.12 (56.32)	8.68 (8.30)	35.2 (35.38)	–
HL′	$C_{20}H_{27}N_7O$ (381)	Yellow 72	181.5 ± 0.5 -	63.24 (62.99)	7.19 (7.09)	25.37 (25.72)	–
HL″	$C_{20}H_{26}N_7OBr$ (459.9)	Light yellow 70	173.5 ± 0.5 -	51.99 (52.18)	5.94 (5.65)	21.21 (21.31)	–
[CoL′$_2$]	$(C_{20}H_{26}N_7O)_2Co$ (818.9)	Purple 29	208.0 ± 1.0 4.12	58.92 (58.62)	6.65 (6.35)	23.83 (23.93)	6.69 (7.19)
[CoL″$_2$]	$(C_{20}H_{25}N_7BrO)_2Co$ (976.7)	Deep purple 40	250.5 ± 0.5 4.27	49.45 (49.15)	5.22 (5.12)	19.77 (20.07)	5.93 (6.03)
[NiL′$_2$]	$(C_{20}H_{26}N_7OCl)Ni$ (474.2)	Green 82	199.2 ± 0.8 Diamagnetic	50.41 (50.61)	5.28 (5.48)	20.91 (20.67)	12.54 (12.38)
[NiL″$_2$]	$(C_{20}H_{25}N_7BrOCl)Ni$ (553.1)	Light green 87	201.2 ± 0.8 Diamagnetic	43.14 (43.39)	4.92 (4.52)	17.90 (17.72)	10.28 (10.61)
[CuL′$_2$]	$(C_{20}H_{26}N_7O)_2Cu$ (823.5)	Dark green 41	194.0 ± 1.0 1.82	58.48 (58.29)	6.07 (6.31)	24.15 (23.80)	7.41 (7.71)
[CuL″$_2$]	$(C_{20}H_{25}N_7BrO)_2Cu$ (981.3)	Green 45	214.0 ± 1.0 1.78	48.49 (48.91)	5.38 (5.10)	20.32 (19.97)	–

TABLE-2
KEY IR BANDS (cm^{-1}) AND ELECTRONIC SPECTRAL DATA (cm^{-1}) (ε_{max} M^{-1} cm^{-1}) OF HIDRAZONE DERIVATIVES AND THEIR METAL COMPLEXES

Compound	ν(OH)	ν(NH)	ν(CH=N-CH) s-triazine rings	ν(CH=N)	ν(M-O)/ ν(M-N)	ν(M-Cl)	Charge transfer ($\varepsilon \times 10^4$)	Imine $\pi \rightarrow \pi$ ($\varepsilon \times 10^4$)	$d \rightarrow d^*$ ($\varepsilon \times 10^4$)
L	–	3412 3325*	1575	–	–	–	240 (12)* 273 (99)*	–	–
HL′	3386	3071	1576	1649	–	–	275 (1.2)	324 (1.8)	–
HL″	3442	3276	1575	1673	–	–	279 (1.1)	326 (1.6)	–
[CoL′$_2$]	3450	3071	1562	1628	508/463	–	327 (2.2)	364 (57)	594 (8.9) 677 (0.72)
[CoL″$_2$]	3490	3261	1559	1624	496/463	–	324 (2.6)	372 (96)	596 (7.2 675 (1.2)
[NiL′$_2$]	3406	3121	1560	1623	498/458	365	321 (1.2)	361 (14)	466 (53)
[NiL″$_2$]	3406	3117	1560	1629	498/458	365	312 (1.2)	361 (14)	472 (39)
[CuL′$_2$]	3406	3120	1560	1631	498/458	–	318 (1.2)	361 (14)	380 (31) 691 (4.8)
[CuL″$_2$]	3496	3291	1558	1627	–	–	310 (1.9)	370 (15)	387 (57) 697 (8.3)

*NH_2 vibration for.

indicating that these ligands are present in enolic forms (Fig. 3a). The -CH=N- stretching modes in the spectra of all ligands and their complexes are observed in the range of 1689-1649 cm^{-1}.



R'

enol form
a

keto form
b

Fig. 3. Keto-enol tautomerism

^1H and ^{13}C NMR spectra of the hydrazone derivatives were recorded in DMSO-d_6 (Tables 3 and 4). The ligands (HL′ and HL″) containing -CH=N- and -OH groups on adjacent carbons can exhibit keto-enol tautomerism[16]. The ligands show signals at 8.12-8.56 ppm which are attributed to the imine protons (-N=CH-). Signals at 10.90-11.12 ppm and at 11.73-12.83 ppm are assigned to the NH and OH protons, respectively for HL′ and HL″. These data strongly suggest that even in solution the enol forms remain as dominant species (Fig. 3a). Similar behaviour was previously reported for other hydrazone derivatives[17].

The downfield shift of NH protons may be due to involvement of this group with a hydrogen bond in DMSO-d_6, which is well known for its interaction with an amide proton[18]. The multiplets within the 6.70-7.96 ppm range are assigned to the aromatic protons of both rings[19]. In ^1H NMR spectra of HL′ and HL″ all imine protons appear as singlets.

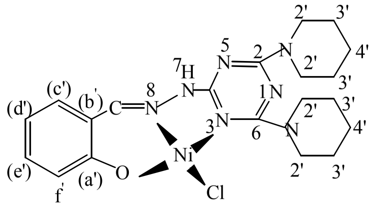
Since Co(II) and Cu(II) complexes are paramagnetic, the ^1H NMR spectra could not be obtained. The ^1H NMR spectra of the diamagnetic Ni(II)[20], which have not been expected for d^4 complexes, however, were obtained. The signals (^1H NMR and IR spectra) of Ni(II) complexes are different from those of the corresponding ligands, suggesting the coordination through oxygen atoms in a phenol ring and an azomethine groups[20].

The signals (^1H, ^{13}C NMR and IR spectra) of Ni(II) complexes are different from those of the corresponding ligands, suggesting the coordination through nitrogen atoms in a -s- triazine ring and an azomethine groups[21].

The hydrazone derivatives and their complexes exhibit sharp bands in 1575-1558 cm^{-1}, which are due to -HC=N-CH- stretching vibrations in -s-triazine rings (Table-2)[18]. The bands appear in somewhat lower regions then those for free ligands due to coordination of a s-triazine group with a nickel and chromium ion[22] (Fig. 4b).

TABLE-3
^{1}H NMR SPECTRAL DATA (δ ppm) OF HYDROZONES DERIVATIVES AND THEIR NICKEL(II) COMPLEXES

Labelling number	L	HL′	HL″	[NiL′]	[NiL″]
2′	3.79 (s, 8H)	3.62 (s, 8H)	3.51 (s, 8H)	3.61 (s, 8H)	3.51 (s, 8H)
3′	1.60 (s, 8H)	1.39 (s, 8H)	1.30 (s, 8H)	1.38 (s, 8H)	1.31 (s,8H)
4′	1.63 (s, 4H)	1.51 (s, 4H)	1.42 (s, 4H)	1.52 (s, 4H)	1.41 (s, 4H)
7	5.89 (s, 1H)	11.12 (s, 1H)	11.07 (s, 1H)	10.99 (s, 1H)	11.10 (s, 1H)
8	3.96 (s, 2H)	8.12 (s, 1H)	8.19 (s, 1H)	7.97 (s, 1H)	7.99 (s, 1H)
a	–	12.07 (s, br, 1H)	11.73 (s, br, 1H)	-	-
Aromatic protons	–	6.79-7.24 (m, 4H)	6.70-7.30 (m, 3H)	6.72-7.20 (m, 4H)	6.76-7.33 (m, 3H)



s = singlet; d = doublet; m= multiplet; br = broad.

TABLE-4
^{13}C NMR SPECTRAL DATA (δ ppm) OF HYDROZONES DERIVATIVES AND THEIR NICKEL(II) COMPLEXES

Labelling number	L	HL′	HL″	[NiL′]	[NiL″]
2, 6	166.61	164.71	164.83	164.71, 164.57	164.73, 164.59
4	167.36	164.44	164.43	164.34	164.27
8	–	158.11	158.24	157.21	157.31
a′	–	136.09	136.09	136.92	136.71
b′	–	131.07	132.09	131.11	132.12
c′-f′	–	120.27-129.90	119.27-131.11	120.28-129.91	120.27-130.11
2′	46.61	44.44	44.43	44.31	44.34
3′	27.17	25.23	25.21	25.19	25.16
4′	25.96	26.29	26.27	26.27	26.28

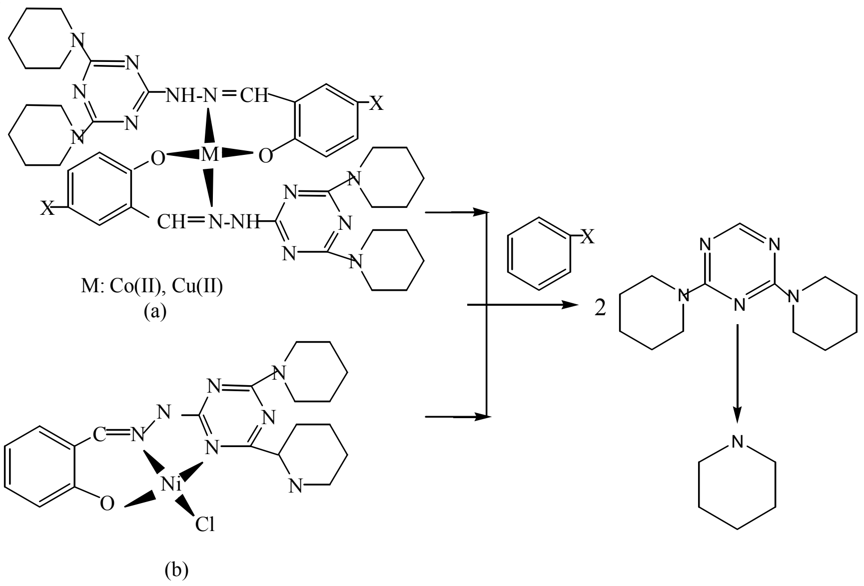


Fig. 4. Mass fragmentation of the complexes

The -CH=N- streching modes of the complexes appear in the range of 1631-1624 cm^{-1} and in somewhat lower regions than those observed for free ligands. This suggests coordination through azomethine nitrogen atoms[23]. There are not show shift at ν(NH) bands in the complexes lending further support to the suggestion that the atoms NH in the >C=N-NH-C< do not coordinate with the metal ion[24].

The Ni(II) complexes exhibits signals in the range of 11.10-10.99 ppm due to NH protons. The -N=CH-C= peak of the complexes are observed in the range of 7.99-7.97 ppm and in a higher field than that observed for ligands. The ligands can coordinate Ni(II) ions with deprotonated phenolic oxygen[22] (Fig. 4b). HL′ and HL″ showed broad signals at 12.83-12.07 ppm but the complexes do not contain OH signals. ^{13}C NMR spectra of the ligands were assigned by comparison with those of their Ni^{2+} complexes. The signals of carbon atoms which neighbour to an OH group are differently observed. This can be attributed to coordination of the phenolic oxgen atom[23]. In the ^{13}C NMR spectra of the ligands the peaks at in the range of 164.83-164.43 ppm correspond to two C atoms in the same position (*i.e.*, position 2 and position 6). In the ^{13}C NMR spectra of the Ni(II) complexes new weak peaks appear at 164.57 and 164.59 ppm. This behaviour can be due to coordination of the nitrogen atom in s-triazine ring. ν(CH=N) modes shift to lower frequencies in IR spectra and the new peaks in the region of 508-496 and 461-458 cm^{-1} is assigned to ν(M-O) and ν(M-N)[24].

Analysis by LC-Mass spectroscopy gave the molecular ion of the hydrazone derivatives at the desired position m/z: 317 [M+H$^+$], 332 [M+2H$^+$] and 342 [M-8H$^+$]; respectively for the HL′ and HL″. LC mass spectra for the give [M]$^+$ 474 (m/z = % 2.8), [M]$^+$ 553 (m/z = % 3.8), for [NiL'], [NiL"], respectively. These results indicate the monomeric nature of the Ni(II) complexes.

The results indicate the dimeric nature of Co(II) and Cu(II) complexes according to the LC-Mass spectroscopy [M+H]$^+$ 819.9 (m/z: % 2.2), [M+H]$^+$ 977.7 (m/z : % 3.8), [M-3H]$^+$ 820.5 (m/z: % 4.4), [M-2H]$^+$ 979.3 (m/z: % 1.6), for [CoL′$_2$], [CoL″$_2$], [CuL′$_2$], [CuL″$_2$]; respectively).

The major fragmentation pathways are followed by the molecular ion of complexes, as shown Fig. 4. Includes an ion peak of strong intensity (100, 68 %) at m/z : 246, 84 and may be ascribed to the resulting from the elimination of the C_6H_5X (X: H, Br) fragment.

The significant electronic spectra of the complexes recorded in DMF are presented in Table-2. The important bands of the ligands and the complexes are observed in the region of 362-270 and 372-324 nm. They may be attributed, respectively, to $\pi \rightarrow \pi^*$ (imine) type and charge-transfer transitions[19].

The electronic spectra of the copper(II) complexes shows two *d-d* bands at *ca.* 665 and 380 nm, respectively, the positions of which are an indication of square-planar stereochemistry[25]. The observed high magnetic moments for the square-planar complexes compared with the values for the distorted octahedral complexes may be taken as additional evidence for the presence of square-planar geometry around the copper(II) ion. More intense bands in the *d-d* electronic spectra due to $^3T_1(F) \rightarrow {}^3T_1(P)$ transition and high magnetic moment values support a tetrahedral configuration for the cobalt(II) complexes[26,27]. For the nickel(II) complexes, absorption at 490 nm, which is assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, is consistent with a D_{4h} symmetry about the metal[27].

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