

Available online at www.sciencedirect.com



SPECTROCHIMICA ACTA PART A

Spectrochimica Acta Part A 62 (2005) 1188-1195

www.elsevier.com/locate/saa

Synthesis and spectroscopic studies of copper(II) and nickel(II) complexes containing hydrazonic ligands and heterocyclic coligand

Ramazan Gup*, Bülent Kırkan

Department of Chemistry, Mugla University, 48000 Kotekli-Mugla, Turkey

Received 28 March 2005; received in revised form 14 April 2005; accepted 19 April 2005

Abstract

Two types of copper(II) and nickel(II) complexes derived from benzophenone anthranoylhydrazone (L_1), 2-acetonaftanone anthranoylhydrazone (L_2), 4-phenylacetonaftanone anthranoylhydrazone (L_3), benzophenone salicyoylhydrazone (L_4), 2-acetonaftanon salicyoylhydrazone (L_5), 4-phenylacetonaftanon salicyoylhydrazone (L_6) and bidentate heterocyclic base [1,10-phenanthroline (phen)] with general stoichiometry [ML₂] and [ML(phen)]Cl have been synthesized and characterized by elemental analysis, infrared spectra, UV–vis electronic absorption spectra and magnetic susceptibility measurements. The effect of varying pH and solvent on the absorption behavior of both ligands and complexes have been investigated. According to the IR spectra, the ligands act as monobasic bidentate and coordination takes place in the enol tautomeric form.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Schiff base; Aroyl hydrazone; Mixed ligand; IR and electronic spectra; Copper(II) and nickel(II) complexes

1. Introduction

Benzoylhydrazones of aldehydes and ketones have a set of different bonding sites and form stable complexes with various transition metal ions differing in the composition, structure and properties [1-7]. Both hydrazones and their coordination compounds present a great variety of biological activity. A number of hydrazones and their metal complexes have been synthesized and reported to exhibit biological activity [8-12] so far. Aromatic ketone derivatives of anthranoylhydrazones and salicyoylhydrazones are potential ligands owing to their variable bonding sites. Furthermore, abilities to coordinate to metals either in keto(I) or enol(II) tautomeric form make them attractive as ligands. 1,10-Phenanthroline (phen) is widely used as the classical N,N'-bidentate ligand to prepare mixed-ligand complexes in coordination chemistry. The mixed-ligand structure can cause to be different in bonding, spectral properties and geometry in coordination compounds.

In this paper, we report the synthesis and characterization of benzophenone, 2-acetonaftanone, 4-phenylacetonaftonone anthranoylhydrazones and salicyloylhydrazone and their copper(II) and nickel(II) complexes [ML₂] as well as mixed-ligand complexes with 1,10-phenanthroline [ML(phen)]Cl. The effect of varying pH and solvent upon the absorption ability of Schiff base derivatives and their complexes is also discussed in more detail.

2. Experimental

2.1. Reagents

All the chemicals used were of AR grade. Benzophenone, 2'-acetonaphthone, 4-acetylbiphenyl, methyl anthranilate, ethyl salicylate and hydrazine monohydrate were purchased from Merck and Aldrich and used without further purification.

2.2. Apparatus

¹H NMR spectra were recorded on a Bruker 200 MHz spectrometer in DMSO_d₆ with TMS as the internal standard.

^{*} Corresponding author. Tel.: +90 252 2111496; fax: +90 252 2238656. *E-mail address:* rgup@mu.edu.tr (R. Gup).

^{1386-1425/\$ –} see front matter 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2005.04.015

IR spectra were recorded on a Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. The electronic spectra of the ligands and complexes were recorded on a UV-1601 Shimadzu spectrophotometer in various solvents. Magnetic susceptibility measurements were performed at room temperature by Faraday method using Hg[Co(SCN)₄] as a calibrent. Atomic absorption spectrophotometer used to determine metal ion concentration in the aqueous phase was DV 2000 Perkin Elber ICP-AES. Melting points were determined on an Electrothermal IA 9100 digital melting point apparatus and are uncorrected.

2.3. Synthesis of ligands

Salicyloylhydrazine and anthranoylhydrazine were prepared by refluxing ethyl salicylate (10 mmol, 1.48 mL) or ethyl anthranilate (10 mmol, 1.48 mL) with hydrazine hydrate (2.5 mL) for 4 h, respectively [3,13,14]. The compounds separated on standing over night, filtered and washed with distilled water. The pure hydrazines were obtained by recrystalliztion from hot ethanol.

The ligands synthesized in this work are shown in Scheme 1 and their syntheses are described as follows.

Anthranoylhydrazine (10 mmol, 1.51 g) or salicyloylhydrazine (10 mmol, 1.52 g) dissolved in hot ethanol (30 mL) was added to solution of benzophenone, (10 mmol, 1.82 g), 2'-acetonaphthone (10 mmol, 1.70 g) and 4-acetylbiphenyl (10 mmol, 1.96 g) with an equivalent amount of glacial acetic acid in ethanol (30 mL). The reaction mixture was stirred while refluxing for 2 h and left over night. The crystalline compounds were filtered off and washed several times with cold ethanol and dried in at room temperature (Scheme 1). Some properties of the synthesized ligands and complexes are given in Table 1.



Scheme 1. (i) $NH_2NH_2 \cdot H_2O$ reflux 4 h and (ii) 4-chloroacetophenone, benzophenone, 2'-acetonaphthone or 4-acetylbiphenyl, EtOH, CH_3COOH , reflux 2 h. Ligands referred to here are $L_1 = X$: $-NH_2$, Ar: $C_6H_5 -$, Ar': $C_6H_5 -$; $L_2 = X$: $-NH_2$, Ar: $CH_3 -$, Ar': $C_{10}H_7 -$; $L_3 = -NH_2$, Ar: $CH_3 -$, Ar': $C_{12}H_9 -$; $L_4 = X$: -OH, Ar: $C_6H_5 -$, Ar': $C_6H_5 -$; $L_5 = X$: -OH, Ar: $CH_3 -$, Ar': $C_{10}H_7 -$; $L_6 = X$: -OH, Ar:: $CH_3 -$, Ar': $C_{12}H_9 -$.

2.4. Synthesis of complexes

2.4.1. Synthesis of $[Cu(L)_2]$ and $[Ni(L)_2]$

To hot solution of the ligands (10 mmol) in 20 mL of methanol, the metal(II) acetates (5 mmol) in 10 mL of methanol were added. The reaction mixture was heated under reflux for 2 h and then the volume was reduced to half of the initial volume under reduced pressure. The separated precipitates were filtered off, washed with water, ethanol and finally diethyl ether and then dried in air at room temperature.

2.4.2. Synthesis of [CuL(phen)]Cl and [NiL(phen)]Cl

The complexes [ML(phen)]Cl were prepared by the following general method. To a solution of $CuCl_2 \cdot 2H_2O$ or NiCl_2 $\cdot 6H_2O$ (10 mmol) in methanol (10 mL), a solution of 1-10-phenanthroline (phen) (10 mmol) in 10 mL methanol was added dropwise with constant stirring. The resulting colored solution which was suspension in the case of copper complexes was stirred and heated for 15 min. To this, 10 mmol ligands dissolved in hot methanol was added and refluxed for 2 h. The colored precipitates were filtered, washed with water, ethanol and finally with diethyl ether and then dried in at room temperature.

3. Results and discussion

Hydrazones such as synthesized in this work may exit in the keto(I) or in the enol(II) tautomeric form in the solid state (Fig. 1). The observation of strong v(C=O) absorption bands around 1641–1667 cm⁻¹ in the infrared spectra of the ligands suggest that the ligands are in the keto form in the solid state [5,8,15,16]. The tautomeric keto forms of compounds were also indicated by ¹H NMR spectroscopy since OH signals of enol forms of ligands were not observed while amide NH signal of keto forms appeared around 10.47–11.01 ppm.

3.1. ¹H NMR data for the ligands

In the ¹H NMR spectra of the anthranilic acid hydrazone derivatives L_1 , L_2 and L_3 , the NH proton bonded to two unsaturated nuclei appears as a singlet at 10.68 ppm for L_1 , 10.47 ppm for L_2 and 10.80 ppm for L_3 . The singlet peak appeared around 6.34–6.47 ppm is assigned to $-NH_2$ protons. The other obtained values for ¹H NMR chemical shifts of these compounds are given Table 2. These data are in agreement with previously reported for similar compounds [2,17–19].

In the ¹H NMR spectra of the ligands derived from salicyloylhydrazine and ketones L₄, L₅ and L₆, the phenolic OH and amide NH resonances appear as a singlet at δ 12.03 and 11.55 ppm for L₄, 11.98 and 12.44 ppm for L₅ and 12.10 and 11.60 ppm for L₆. The movements of phenolic OH proton absorptions to lower frequency can be explained by strong intramolecular hydrogen bonding in these compounds

 Table 1

 Elemental analytical results and some properties of the ligands and complexes

Complex	Empiric formula	mp (°C)	Yield (%)	B.M. (μ_{eff})	Calculated (found)			
					C	Н	Ν	М
L ₁	C ₂₀ H ₁₇ N ₃ O	150	87	_	76.20 (75.92)	5.40 (5.31)	13.30 (12.98)	_
1	C40H32N6O2Cu	257	79	1.79	69.46 (69.23)	4.63 (4.86)	12.15 (11.89)	9.11 (9.54)
2	C32H24N5OCuCl	>300	77	1.94	64.86 (65.01)	4.05 (3.86)	11.82 (11.66)	10.64 (10.93)
3	C40H32N6O2Ni	234	78	2.98	69.97 (70.14)	4.66 (4.31)	12.24 (12.64)	8.45 (8.19)
4	C32H24N5ONiCl	>300	76	3.14	65.40 (65.73)	4.08 (3.90)	11.92 (11.68)	9.88 (10.11)
L ₂	C ₁₉ H ₁₇ N ₃ O	196	86	_	75.25 (75.55)	5.61 (5.83)	13.86 (14.08)	_
5	C38H32N6O2Cu	211	89	1.68	68.36 (68.20)	4.79 (4.54)	12.60 (12.92)	9.44 (9.12)
6	C31H24N5OCuCl	233	74	1.78	64.13 (64.50)	4.13 (4.33)	12.06 (11.79)	10.86 (11.01)
7	C38H32N6O2Ni	315	83	2.96	68.88 (68.73)	4.83 (4.88)	12.68 (12.67)	8.76 (8.83)
8	C ₃₁ H ₂₄ N ₅ ONiCl	278	76	3.12	64.69 (64.47)	4.17 (4.30)	12.17 (12.40)	10.08 (9.89)
L ₃	C ₂₁ H ₁₃ N ₃ O	248	84	_	76.59 (76.44)	5.77 (5.91)	12.76 (12.53)	_
9	C42H36N6O2Cu	223	81	1.76	70.10 (69.80)	5.00 (5.11)	11.68 (11.43)	8.76 (8.99)
10	C ₄₂ H ₃₆ N ₆ O ₂ Ni	324	73	1.80	70.39 (70.56)	5.04 (4.91)	11.76 (11.50)	8.12 (8.30)
11	C33H26N5OCuCl	198	77	2.69	65.34 (65.21)	4.30 (4.08)	11.55 (11.80)	10.40 (10.12)
12	C33H26N5ONiCl	310	75	2.76	65.89 (66.06)	4.32 (4.51)	11.65 (11.30)	9.65 (9.42)
L_4	$C_{20}H_{16}N_2O_2$	225	76	_	75.95 (75.66)	5.06 (4.92)	8.86 (8.60)	_
13	$C_{40}H_{30}N_4O_4Cu$	232	83	1.68	69.26 (68.76)	4.33 (3.83)	8.08 (7.98)	9.09 (9.28)
14	C32H23N4O2CuCl	240	86	1.87	64.75 (64.49)	3.87 (3.99)	9.44 (9.21)	10.62 (10.84)
15	C40H30N4O4Ni	268	78	2.61	69.76 (70.01)	4.36 (4.53)	8.15 (7.99)	8.44 (8.60)
16	$C_{32}H_{23}N_4O_2NiCl\\$	348	71	2.95	65.30 (65.75)	3.91 (3.57)	9.52 (9.38)	9.86 (9.57)
L ₅	$C_{19}H_{16}N_2O_2$	244	80	_	74.51 (74.77)	5.88 (6.00)	9.15 (9.33)	-
17	C38H30N4O4Cu	250	72	1.96	68.16 (68.40)	4.48 (4.29)	8.37 (8.56)	9.41 (9.20)
18	C31H23N4O2CuCl	198	70	1.87	64.02 (63.80)	3.95 (4.12)	9.64 (9.49)	10.84 (10.67)
19	C38H30N4O4Ni	>300	76	2.80	68.67 (68.55)	4.52 (4.30)	8.43 (8.70)	8.73 (9.02)
20	$C_{31}H_{23}N_4O_2NiCl \\$	285	73	2.77	64.58 (64.36)	3.99 (3.76)	9.72 (9.54)	10.06 (9.89)
L ₆	$C_{21}H_{18}N_2O_2$	230	87	_	76.36 (76.60)	5.45 (5.31)	8.48 (8.71)	-
21	C42H34N4O4Cu	245	81	1.63	69.90 (69.67)	4.71 (4.59)	7.76 (7.99)	8.73 (9.00)
22	C33H25N4O2CuCl	215	79	1.74	65.23 (65.66)	4.12 (4.34)	9.22 (9.50)	10.37 (10.03)
23	C ₄₂ H ₃₄ N ₄ O ₄ Ni	211	83	2.78	70.39 (70.09)	4.75 (4.59)	7.82 (7.99)	8.10 (7.89)
24	$C_{33}H_{25}N_4O_2NiCl\\$	302	80	2.90	65.78 (65.61)	4.15 (3.99)	9.30 (9.56)	9.63 (9.89)



Fig. 1. Tautomeric forms of the ligands.

Table 2				
¹ H NMR s	pectra da	ta of the l	igands, δ	(ppm)

Complex	ОН	NH	Aromatic proton	$-NH_2$	-CH ₃
L ₁	-	10.68 (s, 1H)	6.73–7.89 (m, 14H)	6.34 (s, 2H)	_
L ₂	_	10.47 (s, 1H)	6.81-8.01 (m, 11H)	6.40 (s, 2H)	2.48 (s, 3H)
L ₃	_	10.80 (s, 1H)	6.97-8.17 (m, 13H)	6.47 (s, 2H)	2.63 (s, 3H)
L ₄	12.03 (s, 1H)	11.55 (s, 1H)	6.82-7.90 (m, 14H)	_	-
L ₅	11.98 (s, 1H)	11.44 (s, 1H)	6.77-8.10 (m, 14H)	-	2.40 (s, 3H)
L ₆	12.10 (s, 1H)	11.60 (s, 1H)	6.89–7.96 (m, 13H)	_	2.59 (s, 3H)



Fig. 2. Intramolecular hydrogen bonding of L₄, L₅ and L₆.

[14,17,20] (Fig. 2). The other proton resonances of these ligands are given in Table 2.

3.2. IR spectra of the ligands

In the IR spectra of hydrazone compounds, the characteristic amide I band is observed at $1667-1641 \text{ cm}^{-1}$. The absorption bands appearing at $1633-1604 \text{ cm}^{-1}$ are assigned to the stretching vibration of >C=N group. In the case of salicyloylhydrazone derivatives, a very broad medium intensity peak is observed at $3200-2600 \text{ cm}^{-1}$ region which are assigned to the intramolecular H-bonding vibration (O-H···O) [14,16] (Fig. 2). Also the amide NH stretching bands of these compounds were not observed in the IR spectra probably due to overlapping with intramolecular hydrogen bonded OH stretching frequencies. For derivatives of salicyloylhydrazone, two isomers that have intramoleculer hydrogen bonding can be possible (Fig. 2). When the IR spectra of anthranoylhydrazone derivatives are compared with those of salicyloylhydrazone derivatives, it is seen that the ν (C=O) stretching vibrations of L₄, L₅ and L₆ appear at lower frequency $(1641-1648 \text{ cm}^{-1})$ than those of $(1663-1667 \text{ cm}^{-1})$ of L_1, L_2 and L_3 . This phenomena may be explained that the carbonyl groups of salicyloylhydrazone derivatives bond to the phenolic OH group by intermolecular hydrogen bonding. Therefore, the isomer II is more suitable owing to the position of strong intermolecular hydrogen bonding (O–H…O) (Fig. 2). In the case of IR spectra of anthranoylhydrazone derivatives, the peaks observed at 3472-3463 and 3356-3346 cm⁻¹ are attributed to symmetric and asymmetric stretching vibrations of the NH₂ group. The amide NH stretching vibrations are observed around $3190 \,\mathrm{cm}^{-1}$. The other characteristic IR peaks of hydrazone compounds synthesized in this work are given in Table 3. These values are in accord with the previously reported hydrazone derivatives [1–5,14–18].

3.3. IR spectra of the complexes

The IR spectra of the complexes presented in Table 3 show significant differences from the free ligand. The bands due to amide I ν (C=O), ν (C=N_{imine}) and amide ν (NH) are

absent in the IR spectra of the complexes, but two new bands appear between 1615–154 and \sim 1150 cm⁻¹, probably due to >C=N-N=C< and C-O, respectively, suggesting that the NH proton is lost via enolazition and the resulting enolic oxygen and the azomethine nitrogen take place in coordination [4-7] The movement of ν (N–N) stretch of the complexes to higher energy by \sim 30–35 cm⁻¹ compared to that of free ligand can be another evidence for the involvement of azomethine nitrogen in coordination. The symmetric and asymmetric stretching vibrations of amino group $\nu(NH_2)$ of anthranoylhydrazone derivatives are observed almost at the same position with those of free ligands indicating their non-involvement on coordination [2,3,7]. The IR spectra of complexes derived from L₄, L₅ and L₆ show a broad band around $3450 \,\mathrm{cm}^{-1}$ which can be attributed to the free OH stretch indicating nonparticipation of phenolic OH group in coordination.

3.4. Magnetic studies

The magnetic moment data of the solid state complexes at room temperature are reported in Table 1. The magnetic moment values of the copper complexes 1.63–1.96 B.M. corresponds to the spin value for one unpaired electron, indicating these complexes are monomeric. No definite information can be concluded regarding the coordination geometries of these complexes. All the nickel complexes are paramagnetic and show magnetic moment values in the region of 2.61–312 B.M. According to magnetic values and the elemental analysis results, the nickel(II) complexes have a tetrahedral geometry around Ni(II) ions (Fig. 3).

3.5. Electronic absorption spectra

The electronic spectra for the hydrazone ligands recorded in various solvents such as EtOH, DMF and CHCl₃ are given in Table 4. The effect of pH change for absorption spectra was also performed by adding 0.1 M HCl and KOH. The pH value of all solution used was in the range between basic and acidic. The electronic spectral data of the ligand exhibit 3–4 bands in the UV region. The band appearing in the range of 238–245 nm is attributed to $\pi \rightarrow \pi^*$ transition

Table 3
IR spectral data for the ligands and complexes (KBr, cm ⁻¹)

Complex	NH ₂ /OH	NH	C=O	C=N	C=N-N=C	C-N/C-O	N—N
L ₁	3468, 3360	3200	1663	1630	_	1323	1028
1	3465, 3350	-	-	-	1615	1318/1163	1023
2	3455, 3340	-	-	-	1610	1315/1158	1054
3	3469, 3345	_	-	-	1609	1320/1160	1049
4	3458, 3328	_	-	-	1614	1315/1162	1051
L ₂	3472, 3356	3193	1667	1628	_	1320	1027
5	3470, 3301	-	-	-	1614	1310/1161	1045
6	3469, 3352	-	-	-	1610	1314/1162	1050
7	3465, 3358	-	-	-	1608	1315/1160	1051
8	3449, 3338	_	_	_	1612	1313/1155	1055
L ₃	3471, 3359	3190	1659	1633	_	1325	1030
9	3467, 3349	-	-	-	1608	1320/1167	1059
10	3460, 3334	-	-	-	1605	1317/1165	1063
11	3455, 3330	_	_	_	1609	1323/1155	1058
12	3461, 3338	_	_	_	1614	1315/1149	1061
L_4	2563-3222	_	1641	1604	_	1233	1026
13	3430	_	_	_	1589	1253, 1149	1062
14	3426	-	-	-	1584	1260, 1178	1055
15	3448	_	_	_	1596	1260, 1156	1057
16	3456	_	_	_	1590	1263, 1143	1051
L ₅	2560-3230	_	1645	1610	_	1255	1025
17	3439	-	-	-	1592	1253, 1149	1049
18	3445	_	_	_	1588	1250, 1145	1055
19	3451	-	-	-	1588	1250, 1158	1053
20	3450	_	_	_	1593	1242, 1160	1050
L ₆	2560-3250	_	1640	1608	_	1250	1028
21	3460	-	-	-	1592	1260, 1163	1049
22	3443	_	_	_	1587	1254, 1158	1056
23	3428	_	_	_	1590	1250, 1155	1060
24	3433	_	-	-	1593	1254, 1163	1058

of the benzenoid moiety of the ligands. The band around 266.5–278 nm can be assigned to intra ligand of $\pi \to \pi^*$ transition. The other two bands observed in the region of 303–311 and 316–341 nm are attributed to $n \to \pi^*$ electronic transitions [2,21–23].

3.5.1. Solvent effect on the electronic spectra of the ligands

The electronic absorption spectra of the compounds were studied in various organic solvents, C_2H_5OH , DMF and CHCl₃. It is observed that the absorption spectra of anthranoylhydrazone derivatives (L_1-L_3) are little influenced by

changing the solvent. However, the λ_{max} of the ligands derived from salicylic hydrazide (L₄–L₆) show slightly red shift in CHCl₃ than those of in other solvents, for example compound L₄ 323 nm in CHCl₃, 318 nm in EtOH and 316 nm in DMF (Figs. 4 and 5). Moreover, in the electronic absorption spectra of L₄–L₆, a shoulder around 270 nm which cannot be seen clearly in EtOH and DMF solutions of these ligands becomes more clear in the chloroform solutions.

3.5.2. pH effect on the electronic absorption

The effect of pH change on the electronic absorption spectra of the ligands was studied in EtOH solution by adding a



Fig. 3. Proposed structure of the complexes: (a) [ML₂] and (b) [ML(phen)]Cl and [M=Cu(II) or Ni(II)].

Table 4 Electronic spectral data (nm) of Schiff bases and their complexes

Complex	EtOH	EtOH + HCl	ETOH + KOH	DMF	CHCl ₃
L ₁ 1 2 3 4	242, 296, 347 - - -	240, 295, 345 - - -	238, 296, 346 - - - -	240.5, 297, 268 s, 307 s, 347 240, 264, 300, 311, 346, 361s 241, 265, 274, 301 s, 346, 366s 266, 298, 308 s 345, 373 s 242, 265, 295, 306 s, 345, 356 s	241.5, 297, 343 364, 310, 341, 365 s 265, 276, 296, 309 s, 340, 360 s Insoluble Insoluble
L ₂ 5 6 7 8	242, 278, 306, 341 - - -	238, 278, 306, 336 s - - - -	241, 278, 308, 345 - - - -	242, 267, 280, 312, 347 241, 267, 280, 311, 343, 360 s 267, 276, 312 s, 340, 363 s 267, 310, 339, 445 267, 278, 310 s, 344, 444	243, 271, 279, 311, 336 282, 315 s, 369 243, 276 s, 295 s, 359 Insoluble Insoluble
L ₃ 9 10 11 12	240, 259, 306, 346 - - -	238, 301, 337 s _ _ _ _	240, 277, 306, 346 - - -	267, 310, 343 266, 316, 374 s 244, 266, 277, 308, 361 s 242, 265, 298, 307 s, 337, 380 s 242, 265, 276, 309 s, 338, 386 s	241, 259, 308, 346 262, 312, 338, 371 s 262, 277, 309 s, 339, 374 s Insoluble Insoluble
L ₄ 13 14 15 16	240, 266, 300, 318 - - - -	241, 267, 300, 318 - - - -	243, 303, 313 s, 322 - - - -	239, 259, 263, 299, 317 267, 316, 365 s 266, 276, 297, 366 s 267, 301, 317, 361 s 245, 267, 274, 309 s 360 s	241, 307, 323 255, 317, 354 240, 267, 295, 303 s, 348 s 241, 325, 359 Insoluble
L ₅ 17 18 19 20	240, 273, 282, 313 - - -	242, 270, 281, 315 - - -	242, 273 s, 282, 306, 353 - - - -	242, 267, 285, 316 240, 266, 290, 314, 383 s 267, 276, 300 s, 313, 372 s 266, 292, 363 s 272, 315, 375	241, 275, 281, 322 270, 280, 312, 359 242, 276, 282, 313, 355 Insoluble Insoluble
L ₆ 21 22 23 24	242, 271, 304 s, 319 - - -	241, 280, 305, 317 - - -	242, 309, 352 - - -	248 267, 319 239, 266, 300, 355 s 242, 266, 304 380 s 266, 299 s, 315 s, 363 s 265, 277, 300 s, 313, 369 s	240, 291, 322 265, 295, 316, 359 240, 266, 276, 296, 317, 360 Insoluble Insoluble

small amount of 0.1 M HCl and KOH. The λ_{max} of the salicyoylhydrazone derivatives (L₄, L₅ and L₆) in ethanolic solutions are not effected by adding a small amount of 0.1 M HCl. However, the electronic absorption spectra of these compounds change considerably when adding a small amount of 0.1 M KOH in ethanolic solution. After adding two drops of 0.1 M KOH to ethanolic solution of these ligands, the band appearing around 318 nm in the spectra of the neutral ethanolic solutions of ligands becomes shoulder and the intensity of



Fig. 4. Electronic absorption spectra of L_2 in: (a) EtOH; (b) $CHCl_3$ and (c) DMF.



Fig. 5. Electronic absorption spectra of L_4 in: (a) EtOH; (b) $CHCl_3$ and (c) DMF.



Fig. 6. Electronic absorption spectra of L_4 in: (a) EtOH; (b) EtOH + HCl and (c) EtOH + KOH.

this band slightly decreases with a slight blue shift. Furthermore, a new broad band appears around 352–362 nm indicating that ligands L_4-L_6 exist in the anionic form in basic solutions probably due to phenolic group. The absorption spectra of the hydrazone compounds derived from anthranilic acid hydrazine (L_1-L_3) are not changed by adding 0.1 M KOH with respect to the absorption spectra in ethanol. Furthermore, the λ_{max} of these compounds in ethanol do not show considerable hypsochromic effects when 0.1 M HCl was added (Fig. 6, Table 4).

3.6. Electronic absorption spectra of the complexes

Electronic absorption spectra of $[ML_2]$ and [ML(phen)]Cl complexes were recorded in DMF and CHCl₃ solutions (Table 4). In the electronic spectra of all complexes, there is a band around 350–385 nm which is usually shoulder tailing into visible region in the spectra of many complexes. This band is assigned as a CT transition (Fig. 7) [2,21]. Surprisingly, the CT transition bands of the nickel(II) complexes of 2'-acetonaphthone anthranoylhydrazone (**7** and **8**) which are insoluble in CHCl₃ shows more red shift and appear at 445 and 436 nm, respectively (Fig. 8).

By comparison of the electronic absorption of the free ligands and their complexes, it is observed that the bands appearing around 310 nm for ligands L_1-L_3 and ~300 nm for ligands L_4-L_6 slightly decreases in intensity. In the case of the electronic absorption spectra of the mixed-ligand complexes [ML(phen)]Cl derived from salicyoylhydrazine and aromatic ketones (L_4-L_6), a new shoulder appears around 275 nm which may be attributed to $\pi \rightarrow \pi^*$ transition of phenatranoline moiety of these compounds.

Although the position of CT band of all complexes do not regular variation in DMF and CHCl₃ solvents, it may be



Fig. 7. Electronic absorption spectra of the copper(II) complexes of L_2 in different solvents: (a) [CuL₂]; (b) [CuL(phen)]Cl in DMF; (c) [CuL₂] and (d) [CuL(phen)]Cl in CHCl₃.



Fig. 8. Electronic absorption spectra of L_2 and its nickel(II) complexes in DMF: (a) L_2 ; (b) [NiL(phen)]Cl and (c) [NiL₂].

concluded from Table 4 that the CT transition bands in DMF solution usually show a little more red shift than those of in CHCl₃ solutions. Unfortunately, the expected weak d–d transition in the visible region for all complexes cannot be detected even with concentrated solution. It may be lost in the low energy tail of the charge transfer transition [2,22,24,25].

4. Conclusion

The present paper reports on the synthesis, characterization and their electronic absorption spectra of Schiff bases and their copper(II) and nickel(II) complexes. In this investigation, we also provide 12 mixed-ligand copper and nickel complexes by using these synthesized Schiff base and bidentate 1,10-phenanthroline. The observation of strong ν (C=O) absorption bands around 1641–1667 cm⁻¹ in the IR spectra of the ligands indicates that they are in the keto tautomeric form in the solid state. The other evidence of the keto form of the ligands is the appearance of amide NH signals around 10.47–11.01 ppm in the ¹H NMR spectra. However, in the IR spectra of the complexes v(C=O), v(C=N) and v(N-H) stretching vibrations disappears but two new bands are observed at 1615–154 and ~1150 cm⁻¹ due to >C=N–N=N< and C–O stretches, respectively, suggesting that the coordination takes place in enol tautomeric form. Furthermore, the observation of phenolic v(O-H) and $v(NH_2)$ stretching vibration in the IR spectra of the complexes is concluded as non-involements of these groups in coordination.

The results of the varying pH and solvents effect on the absorption ability of Schiff base and their complexes are also discussed in this paper. In the basic solutions, Schiff base derived from salicyoylhydrazine have a considerable red shift while the acidic medium does not effect the absorption abilities of these compounds. It is also observed in this study that the absorption spectra of anthranoylhydrazone derivative (L_1-L_3) are not effected by the pH change. The λ_{max} of the ligands are not considerably changed by varied solvent. In the case of the electronic spectra of the complexes, CT bands are observed around 350–385 nm except the nickel complexes of L_2 . Both types of complexes [ML₂] and [ML(phen)]Cl show very close CT pattern.

References

- T.R. Rao, S. Shrestha, A. Prasad, K.K. Narang, Synth. React. Inorg. Met.-Org. Chem. 32 (2002) 419.
- [2] S. Naskar, S. Biswas, D. Mishra, B. Adhikary, L.R. Falvello, T. Soler, C.H. Schwalbe, S.K. Chattopadhyay, Inorg. Chem. Acta 357 (2004) 4264.

- [3] B. Singh, K.K. Narang, R. Srivastava, Synth. React. Inorg. Met.-Org. Chem. 31 (2001) 1345.
- [4] A. Sreekanth, U.L. Kala, C.R. Nayar, M.R.P. Kurup, Polyhedron 23 (2004) 41.
- [5] M. Calinescu, A. Emandi, I. Şerban, V. Pop, Synth. React. Inorg. Met.-Org. Chem. 33 (2003) 1927.
- [6] R.M. Issa, S.A. Abdel-Latif, H.A. Abdel-Salam, Synth. React. Inorg. Met.-Org. Chem. 31 (2001) 95.
- [7] P.B. Sreeja, M.R.P. Kurup, A. Kishare, C. Jasmin, Polyhedron 23 (2003) 575.
- [8] E.W. Ainscough, A.M. Brodie, W.A. Denny, G.J. Finlay, S.A. Gothe, J.D. Ranford, J. Inorg. Biochem. 77 (1999) 125.
- [9] N. Nawar, M.A. Khattab, N.M. Hosny, Synth. React. Inorg. Met.-Org. Chem. 29 (1999) 1365.
- [10] Z.H. Chohan, Synth. React. Inorg. Met.-Org. Chem. 31 (2001) 1.
- [11] K. Pihlaja, M.F. Simeonov, F. Fülöp, J. Org. Chem. 62 (1997) 5080.
- [12] D. Van Reyk, S. Sarel, N. Hunt, Biochem. Pharmacol. 60 (2000) 581.
- [13] S.G. Komurcu, S. Rollas, M. Ulgen, J. Gorrod, Boll. Chim. Farm. 134 (1995) 375.
- [14] F.V. Bagrov, T.V. Vasil'eva, Russ. J. Org. Chem. 38 (2002) 1364.
- [15] P.E. Lee, C.T. Yong, D. Fon, J.J. Vittal, J.D. Ranford, Polyhedron 22 (2003) 2781.
- [16] P.W. Sadler, J. Chem. Soc. A (1961) 957.
- [17] L.L. Koh, O.L. Kon, Y.C. Loh, J.D. Ranford, A.L.C. Tan, Y.Y. Tjan, J. Inorg. Biochem. 72 (1998) 155.
- [18] K. Pihlaja, M.F. Simeonov, F. Fülöp, J. Org. Chem. 62 (1997) 5080.
- [19] A.M. Khambekar, A.D. Sawant, Indian J. Chem. 36 (1997) 459.
- [20] J.J. Norman, R.M. Heggie, J.B. Larose, Can. J. Chem. 40 (1962) 1547.
- [21] J.W. Godhes, W.A. Armstrong, Inorg. Chem. 13 (1992) 368.
- [22] D. Maiti, H. Paul, N. Chanda, S. Chakrabort, B. Mondal, V.G. Puranik, G.K. Lahiri, Polyhedron 23 (2004) 831.
- [23] M.M. Rageh, Spectrochim. Acta 60A (2004) 1917.
- [24] E. Prenesti, S. Berto, P.G. Daniele, Spectrochim. Acta 59A (2003) 201.
- [25] S. Pang, Y. Liang, Spectrochim. Acta 57A (2001) 435.