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Synthesis and Characterization of Some New Schiff Base Ligands and Their Complexes with Cobalt(II), Nickel(II) and Copper(II)

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Syntheses of three series of new mononuclear complexes with some new Schiff base ligands have been reported. The new Schiff bases which were used in these complexes were obtained from the Schiff base condensation of 4-nitroaniline and salicylaldehyde and its derivatives (5-bromo-salicylaldehyde, 5-chlorosalicylaldehyde and 4-methoxysalicylaldehyde). The synthesis of these Schiff bases have been performed with acid catalyst and their characterization were explained. In synthesis of these new Shiff bases, we have investigated the effects of different groups on aldehyde and amine in their reactivity in Schiff base condensation reaction was investigated. The study of intramolecular hydrogen bonds is interesting because of the high thermodynamic and structural stability of these systems. The chemical structure of these compounds was confirmed by ^{1}H NMR and IR spectroscopy. The spectroscopic studies of these compounds show significant importance of intramolecular hydrogen bond in their structures.

Key Words: Schiff base, 4-Nitroaniline, Salicylaldehyde, Intramolecular hydrogen bond, Schiff base complexes.

INTRODUCTION

Schiff bases are compounds containing the azomethine group (RC=N–) and are usually formed by the condensation of a primary amine with an active carbonyl compound[1,2]. A large number of Schiff bases and their complexes have been investigated for their interesting and important properties, such as their ability to reversibly bind oxygen, catalytic activity in the hydrogenation of olefins, photochromic properties and complexing ability towards some toxic metals, furthermore complexes of Schiff bases showed promising applications in biological activity and biological modelling applications[3-7].

Schiff base ligands have been extensively studied in coordination chemistry mainly due to their facile syntheses, easily tunable steric, electronic properties and good solubility in common solvents[8]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest because of their ability to possess unusual configurations[9]. Schiff bases can accommodate different metal centers involving various coordination modes allowing successful synthesis of homo- and heterometallic complexes with varied stereochemistry[10]. Additionally, they have wide applications in fields such as antibacterial, antiviral, antifungal agents[11], homogeneous or heterogeneous catalysis[12] and magnetism[13]. Schiff bases are potential anticancer drugs[14] and when administered as their metal complexes, the anticancer activity of these complexes is enhanced comparison to the free ligand[15]. The chemistry of nickel Schiff base complexes has a strong role in bioinorganic chemistry and redox enzyme systems[16].

Cobalt Schiff-base complexes have been used as catalysts for the oxygenation reactions, dioxygen carriers and oxygen activators[17-21] and enantioselective and asymmetric catalysis[22,23]. Modelling of transition metal coordination species existing in living systems and studying of intermediate species involved in reactions of such systems are important investigation fields that attract lots of studies[24].

The chiral Cu complex catalysts for asymmetric reactions such as aziridination[25], Diels-Alder reactions[26], cyclopropanation[27], carbenoid insertion of diazoacetates into the Si-H bond of silanes[28] have been studied and recently the complexes of Cu(II) with chiral bidentate ligands of bisoxazolines for asymmetric Henry reaction have received promising results.

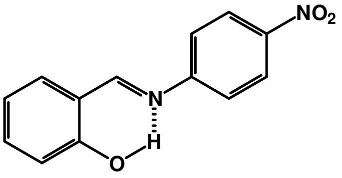
EXPERIMENTAL

All chemicals and solvents were reagent grade and were used without further purification. All the experiments were carried out at room temperature unless otherwise stated. 4-Nitroaniline, salicylaldehyde, 5-bromosalicylaldehyde, 4-methoxysalicylaldehyde and absolute ethanol were obtained from Merck Chemical Co. while 5-chlorosalicylaldehyde was obtained from Acros Co. ^{1}H NMR spectra were recorded on a Bruker Ac-300 spectrometer operating in fourier transform mode. IR spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrophotometre. Melting point was taken on electrothermal digital melting point apparatus 8100 series.

Synthesis of Schiff bases: The following general representative procedure was followed for all of the Schiff bases. The reation time was different between 10 min to 4 h according to the reactivity of the starting materials.

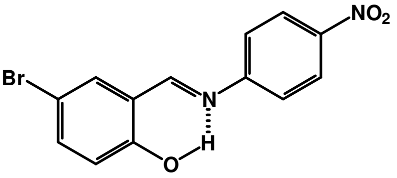
To a solution of 4-nitroaniline (276 mg, 2 mmol) in absolute ethanol (20 mL) was added salicylaldehyde (244 mg, 2 mmol) and one drop of concentrated sulfuric acid as catalyst. The solution was stirred until yellow precipitate was appeared in the reaction mixture. When the reaction was complete (monitored by TLC) the crude product was filtered and recrystallized in the mixture of ethanol and *n*-hexane to give pure Schiff base product.

Preparation of 4-nitrophenylsalycilimine (NPS): Obtained from Schiff base condensation of salicylaldehyde and 4-nitroaniline and collected as a brilliant yellow powder (m.p. 173-174 ºC; yield 68.1 %, reaction time 2 h).



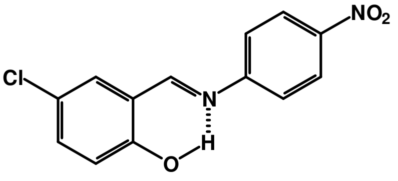
^{1}H NMR (CDCl$_3$) δ: 6.930 (d, 7.2 Hz, 1H), 7.062 (t, 7.8 Hz, 1H), 7.424 (dd, 8.7 and 18.7 Hz, 3H), 7.471(t, 7.5 Hz, 1H), 8.33(d, 9 Hz, 2H), 8.654 (s, 1H), 12.569 (s, 1H). Selected IR bands (KBr, ν_{max}, cm^{-1}): 1615 (C=N),1033 (C-N), 1342 (C-O).

Preparation of (4-nitrophenyl)-5-bromosalicylimin (NPBS): Obtained from Schiff base condensation of 5-bromosalicylaldehyde and 4-nitroaniline and collected as a brilliant orange powder (m.p. 194-196 ºC; yield 77.8 %, reaction time 8 min).



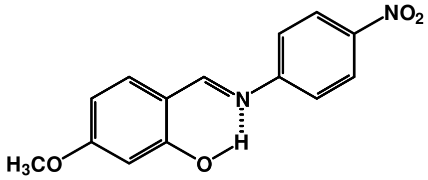
^{1}H NMR (CDCl$_3$) δ: 6.985 (d, 8.7 Hz, 1H), 7.387 (d, 9 Hz, 2H), 7.424 (dd, 2.7 and 8.7 Hz, 1H), 7.579 (d, 2.4Hz, 1H), 8.343 (d, 8.7 Hz, 2H), 8.584 (s, 1H), 12.569 (s, 1H). Selected IR bands (KBr, ν_{max}, cm^{-1}): 1620 (C=N), 1106 (C-N), 1176 (C-Br), 1338 (C-O).

Preparation of (4-nitrophenyl)-5-chlorosalicylaldehyde (NPCS): Obtained from Schiff base condensation of 5-chlorosalicylaldehyde and 4-nitroaniline and collected as a brilliant yellow powder (m.p. 173-174 ºC; yield 72.3 %, reaction time 10 min).



^{1}NMR (CDCl$_3$) δ: 7.025 (d, 8.7 Hz, 1H), 7.364 (d, 3 Hz, 2H), 7.410 (d, 10.5 Hz, 2H), 8.337 (dd, 1.2 and 8.85 Hz, 1H), 8.586 (d, 0.6 Hz, 2H), 12.541 (s, 1H). Selected IR bands (KBr, ν_{max}, cm^{-1}): 1618 (C=N), 1107 (C-N), 1176 (C-Cl), 1337 (C-O).

(4-Nitrophenyl)-4-methoxysalicylaldehyde (NPMS): Obtained from Schiff base condensation of 4-methoxysalicylaldehyde and 4-nitroaniline and collected as a yellow powder (m.p. 143-144 ºC; yield 62.2 %, time of the reaction 4 h).



^{1}H NMR ($CDCl_3$) δ: 3.886 (s, 3H), 6.543 (s, 1H), 6.573 (d, 2.4 Hz, 1H), 7.334 (dd, 1.5 and 6 Hz, 2H), 7.368 (d, 2.1 Hz, 1H), 8.304 (dd, 1.8 and 6.9 Hz, 1H), 8.568 (s, 1H), 13.092 (s, 1H). Selected IR bands (KBr, ν_{max}, cm^{-1}): 1642 (C=N), 1109 (C-N), 1339 (C-O).

Synthesis of Schiff base complexes: The following general procedure was carried out for preparation of 12 Schiff base complexes with three transition metalls Ni(II), Co(II) and Cu(II).

To a solution of 8 × 10^{-1} mmol of Schiff base ligand in 20 mL of hot absolute methanol was added, a solution of 4 × 10^{-1} mmol of $M(AcO)_2 \cdot 4H_2O$ dissolved in 20 mL of hot absolute methanol and the resulting solution was refluxed until the reaction was complete (monitored by TLC). After concentration to one half of the initial volume and cooling down, the product was collected as precipitate. After filteration and washing with chloroform, methanol and acetonitrile, respectively; it was dried under vacuum.

At the following Table-1 some of physical properties of prepared complexes were analyzed.

The ratio of the metal to ligand in the complexes structure has been obtained by atomic absorption technique and for all of the complexes these calculations lead to the 1:2 ratio for metal to ligand.

The IR spectra of the complexes, in comparison with those of the free ligands, display certain changes, which give an idea about the type of coordination and their structure. Significant IR spectral bands of the complexes are listed in Table-2.

RESULTS AND DISCUSSION

The variety of possible Schiff-base metal complexes with a wide choice of ligands and coordination environments, has prompted the present research in this area.

Free Schiff bases show a very strong absorption around 1642-1618 cm^{-1} characteristic of azomethine (>C=N) group[29]. Coordination of the Schiff bases to the metal ion through the azomethine nitrogen atom is expected to reduce the electron density in the azomethine link and thus,

TABLE-1
PHYSICAL PROPERTIES OF PREPARED COMPLEXES

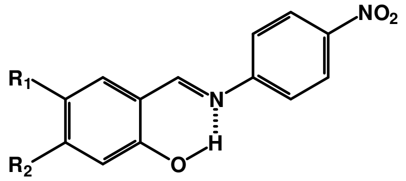
Complexes	m.f.	m.w.	Colour	Decomposition point
$Co(NPS)_2 \cdot H_2O$	$C_{26}H_{20}N_4O_7Co$	561.42	Red	262
$Cu(NPS)_2 \cdot H_2O$	$C_{26}H_{20}N_4O_7Cu$	566.03	Orange	278
$Ni(NPS)_2 \cdot H_2O$	$C_{26}H_{20}N_4O_7Ni$	561.17	Green	272
$Co(NPBS)_2 \cdot H_2O$	$C_{26}H_{18}N_4O_7BrCo$	719.21	Orange	251
$Cu(NPBS)_2 \cdot H_2O$	$C_{26}H_{18}N_4O_7BrCu$	723.82	Brown	256
$Ni(NPBS)_2 \cdot H_2O$	$C_{26}H_{18}N_4O_7BrNi$	718.97	Brown	248
$Co(NPCS)_2 \cdot H_2O$	$C_{26}H_{18}N_4O_7ClCo$	630.31	Orange	264
$Cu(NPCS)_2 \cdot H_2O$	$C_{26}H_{18}N_4O_7ClCu$	634.92	Brown	259
$Ni(NPCS)_2 \cdot H_2O$	$C_{26}H_{18}N_4O_7ClNi$	630.06	Brown	268
$Co(NPMS)_2 \cdot H_2O$	$C_{27}H_{21}N_4O_8Co$	623.48	Red	285
$Cu(NPMS)_2 \cdot H_2O$	$C_{27}H_{21}N_4O_8Cu$	628.10	Orange	287
$Ni(NPMS)_2 \cdot H_2O$	$C_{27}H_{21}N_4O_8Ni$	623.24	Yellow	271

TABLE-2
SELECTED IR SPECTRA DATA OF THE SCHIFF BASE COMPLEXES

Compound	ν(C=N)	δ(OH·H_2O)	ν(C=C)	ν(C-N)	ν(C-O)	γ(OH·H_2O)	ν(M-O)	ν(M-N)
NPS	1614s	–	1483m	1340s	1245m	–	–	400w
$Co(NPS)_2.H_2O$	1604s	1514s	1427m	1341s	1294m	854m	516w	–
$Cu(NPS)_2.H_2O$	1601s	1509s	1438m	1339s	1295m	850m	547w	403w
$Ni(NPS)_2.H_2O$	1607s	1510s	1446m	1341s	1294w	848m	583w	399w
NPBS	1620s	1511s	1470m	1338s	1231w	–	–	–
$Co(NPBS)_2.H_2O$	1602s	1522s	1462m	1339s	1249w	812w	517w	420w
$Cu(NPBS)_2.H_2O$	1604s	1518s	1459s	1340s	1251w	811m	539w	425w
$Ni(NPBS)_2.H_2O$	1606s	–	1456s	1340s	1253w	825m	586w	431w
NPCS	1618s	–	1473m	1337s	1221w	–	–	–
$Co(NPCS)_2.H_2O$	1604s	1512s	1464m	1340s	1248w	812m	518w	424w
$Cu(NPCS)_2.H_2O$	1611s	1522s	1457s	1340s	1249w	826m	566w	430w
$Ni(NPCS)_2.H_2O$	1609s	1520s	1458s	1341s	1245w	826m	587w	419w
NPMS	1642s	–	1483m	1339s	1258m	–	–	–
$Co(NPMS)_2.H_2O$	1617s	1512s	1456m	1336s	1291m	841m	516w	400w
$Cu(NPMS)_2.H_2O$	1618s	1527s	1462	1339s	1295m	817m	547w	403w
$Ni(NPMS)_2.H_2O$	1609s	1531s	1466	1339s	1295w	848m	583w	399w

lower the ν(C=N) absorption frequency. Hence, this band undergoes a shift to lower frequency to 1620-1600 cm^{-1} after complexation, indicating coordination of the azomethine nitrogen to metal[30]. The free ligands exhibit a broad and weak band at 3435-3427 cm^{-1} (because there is an strong intramolecular hydrogen bond in the free ligands structure) which may be assigned to the ν(O-H) and this band is absent in the spectra of all the complexes, conferring the deprotonation of the Schiff base prior to coordination. The hydroxy protons are displaced by the metal leading to higher ν(C–O) (1350-1329 cm^{-1}) compared to that of the free ligands ν(C-O) (1345-1324 cm^{-1}) suggesting that the other coordinating atom is phenolic oxygen[31]. The binding of the metal to the ligand through nitrogen and oxygen atom is further supported by the appearance of new band in 460-400 cm^{-1} and 540-510 cm^{-1} ranges due to ν(M-N) and ν(M-O)[32], respectively, in the spectra of all the complexes.

The Schiff bases derived from salicylaldehyde (Fig. 1) because of intramolecular hydrogen bond are relatively stable[33].



Ligand	R_1	R_2
NPS	H	H
NPBS	Br	H
NPCS	Cl	H
NPMS	H	OMe

Fig. 1. Stabilization of Schiff base by H-bonding

Hydrogen bonding leads to characteristic changes in molecular geometries which are evidences for the formation of hydrogen bonds and can be used as a measure of the strength of these special interactions. Theoretical and experimental studies on these compounds are systematically increasing.

More systematic studies on vibrational spectra as a function of ΔpK_a [$pK(BH^+)$-pK(AH)], in the complex A–CH---B] have shown, however, that the bonding of an intramolecular hydrogen bridge leads to a clear decrease in the strength of hydrogen bonding and consequently to a distinctly smaller red shift of ν(OH)[34]. Another sensitive measure of the strength of hydrogen bonds is the intensity of the ν(OH) band. Two measures of the hydrogen bond strength gave contradictory information. These results can be explained by comparing the dipole moments dependence on the O–CH bond stretching. Schiff bases, because of the more delocalized charge distribution give lower values of the derivatives of dipole moments, which result in intensity[35].

Present study investigates the influence of substituents in phenyl ring and amine used for condensation on the structure of intramolecular hydrogen bond formed in Schiff bases. The first conclusion was as follows: all substituents in phenyl ring, which increase acidity of OH group in applied salicylaldehyde derivatives, promote the proton transfer from oxygen atom to nitrogen and *vice-versa*. These substituents are electron-donating groups in position 4 or electron-withdrawing group in position 3. The second conclusion is, the imine derivatives of aliphatic amines can form intramolecular bridge in which proton is more effectively transferred to nitrogen atom comparing with aromatic amine derivatives. These types of amines have electron-donating groups in position 3 or electron-withdrawing group in position 4.

The IR spectra of the obtained Schiff bases exhibit various bands in the 4000-400 cm^{-1} region. The O–CH stretching frequency of the ligand is expected in the 3800-3300 cm^{-1} region, however, this frequency is generally displaced to the 2960-2840 cm^{-1} region due to the internal hydrogen bonding. As the hydrogen bond becomes stronger, the bandwidth increases, and this band sometimes is not detected as hydrogen bonds in the obtained Schiff bases are usually strong. The obtained molecules are relatively planar with adequate intramolecular distance that favours intramolecular hydrogen bond formation.

These new Schiff bases are considered, it can be noticed that in NPBS the bromo group at position 4 increases the electron density on the hydroxyl group and making the H–O bond stronger and the absorption of H–O bond is on very broad band and cannot be detected in the spectrum.

In the ν(OH) water region, the spectra of synthesized complexes show one relatively strong and sharp band at *ca.* 3440 cm^{-1}, assignable to coordinated water. The presence of H_2O molecules in coordination spheres of these complexes is further confirmed by the appearance of the rocking mode of the aquo ligand at *ca.* 860 cm^{-1}.

^{1}H NMR spectra of the obtained Schiff bases were recorded in $CDCl_3$. The chemical shifts, expressed in ppm downfield from tetramethyl silane. The hydrogen bonded phenolic protons appear as a broad peak between 14 and 12.5 ppm, and the integration is generally less than 1.0 due to this intramolecular hydrogen bonding. As the hydrogen bonds become stronger shift of this peak to weak field will happen and the amount of δ will increase. Thus we can find out that the strongest intramolecular hydrogen bond belongs to NMPS. The region of 7.6-6.8 ppm was assigned chemical shifts for hydrogen of the aromatic ring.

Another effect of electron donation or withdrawing groups on the phenyl ring is appearing at the time of the reactions. The compounds have electron donating group at their *m*-position or electron withdrawing group at their *p*-position will react in a short time to give imines in good to excellent yields. Others react only after a prolonged time and the reaction equilibrium may not be favourable (it may be necessary to remove the formed water to shift the equilibrium towards the imine). Schiff bases are the ones that have electron donating group at their *p*-position or withdrawing group at their *m*-position for example, if the reactivity of 5-bromosalicylaldehyde with 4-methoxysalicylaldehyde towards 4-nitroaniline is compared, it would show that the first one has more reactivity than the second one so it can be concluded that in Schiff base condensation reactions if starting aldehyde has electron donating groups in its 2 or 4 position or if it has electron withdrawing group in its 3 position, it will have a high reactivity while in other case its reactivity is low. On the contrary if starting amine has electron donating groups in its 3 position or if it has withdrawing group in its 2 or 4 positions, it will have a high reactivity.

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