A Density Functional Theory Study of 3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime Complexes with Co, Ni, Cu and Zn Metals

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Summary: In this work, new Schiff baz ligand was synthesized by reaction of *p*-iminoacetophenone oxime with 3,5-dichlorosalicylaldehyde. Metal complexes of Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} acetate metal salts were synthesized with this ligand. The ligand and complexes are characterized in experimental by their elemental analyses, X-ray, ^{1}H-NMR, ^{13}C-NMR, UV-Vis, FT-IR, magnetic susceptibility and thermogravimetric analyses (TGA) and also have been investigated by using quantum mechanical methods. The transition metals are coordinated to the schiff base through the azomethine nitrogen and the carboxyl oxygen atom. Obtained metal complexes were studied the magnetic properties and their geometries were determined. Co^{+2}, Ni^{+2} and Zn^{+2} complexes have been found tetrahedral geometry and Cu^{+2} complex has been found four coordinated geometry.

Key words: Schiff base ligand, Metal complexes, TGA, Coordinated geometry.

Introduction

Schiff bases are easily synthesized from the condensation reaction between the aldehydes and the primary amines [1-3]. Schiff bases are attached to donor atoms located at the building site of the central atom and are known as a good donor ligand. These ligands give one or more electron pairs to the metal ion during the formation of the coordination compound. Schiff bases are among the most used ligands in coordination compounds. The fact that Schiff bases have different properties, the easy synthesis of Schiff-based complexes, increases the interest in these compounds because of their high thermal and chemical stability [4-6]. There are a large number of ligands and complexes in the field of coordination under the roof of modern chemistry, with a wide range of applications. Schiff bases and complexes are used in many fields such as agriculture, pharmaceutical industry, dye industry, plastic industry, liquid crystal technology, industrial applications in polymer technology. In addition, Schiff bases are very important compounds for biological systems. It plays an important role in obtaining essential amino acids for the organism. Some Schiff bases and some of their metal complexes have a considerable precaution due to their antitumor, anticancer and antimicrobial properties [7,8]. In this work, synthesis and characterization of tetrahedral Co(II), Ni(II), Cu(II) and Zn(II) complexes with new 3,5-dichlorosalicylidene-*p*-iminoacetophenone oxime (LH) Metal complexes have been reported to have a tetra-coordinated build-up tendency in the general comparison d^7, d^8, d^9 and d^{10} configurations. The Schiff base ligand synthesized in this work is given in Scheme 1. All compounds were characterized by IR, ^{1}H-NMR, ^{13}C-NMR spectra, UV spectra, thermogravimetric analyzes (TGA) and magnetic susceptibility measurements. In addition, intensity functional theory (DFT) calculations were performed to optimize the structures and to obtain IR and UV spectra of ligand complexes and Co, Ni, Cu and Zn metals.

Experimental

IR spectra were taken with a Mattson 1000 FTIR spectrophotometer at a range of 4000-400 cm^{-1}. Elemental analysis (C, H, N) were performed with the LECO-932 CHNSO model element analyzer. The ^{1}H and ^{13}C-NMR spectra of the Bruker DPX-400 were performed at the TUBITAK with a 400 MHz high performance digital FT-NMR spectrometer. Magnetic suitability measurements were made in room conditions with our current Sherwood Scientific MK1 model magnetic suitability instrument. The TGA spectra were made using the current Shimadzu TGA-50 model thermal analyzer. Electronic spectra were obtained on a Shimadzu 1700 UV spectrometer. All chemicals are supplied from Merck. Hydroxylamine hydrochloride and sodium acetate were used in the synthesis of *p*-aminoacetophenone oxime. 3,5-Dicloxalisilaldehyde was used in the synthesis of the Schiff base. $[M(AcO)_2.nH_2O]$ salts were used in the synthesis of mononuclear complexes of the ligand. Ethanol, diethyl ether and water were used as solvents in the synthesis of

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the complexes and ligand. Resolution tests have been done for all complexes. The complexes were dissolved in DMSO and DMF while partially dissolved in Et_2O, Et_2AcO, MeOH, THF and $CHCl_3$. However, the complexes do not dissolve in apolar organic solvents (n-hexane, benzene) and H_2O.

3,5-dichlorosalicyliden-p-aminoacetophenoneoxime **(LH)**

p-aminoacetophenonoxime (1.50 g, 10 mmol) was dissolved in 10 mL of absolute ethyl alcohol. To this solution was added 3,5-dicloriscalicylaldehyde (1.91 g, 10 mmol) and (0.01 mg) of *p*-toluenesulfonic acid in 40 mL of absolute ethyl alcohol solution. Stirring was continued for 2 hours at 60 °C under reflux. The resulting product was rested overnight at room temperature and filtered. The resulting yellow product was washed with cold ethyl alcohol and diethyl ether and dried in vacuum.

IR spectrum (υ, cm^{-1}): 3394 (oxime O-H), 3238 (phenolic O-H), 1623 (phenolic C=N), 1597 (oxime C=N), 1273 (C-O), 1004 (N-O); ^{1}H-NMR ($CDCl_3$-DMSO-d_6, δ, ppm): 13.09 (s, 1H, phenolic O$\underline{H}$), 10.75 (s, 1H, oxime O$\underline{H}$), 8.62 (s, 1H, azomethine C$\underline{H}$=N), 7.64-6.85 (m, 6H aromatic $\underline{H}$), 1.95 (s, 3H, C$\underline{H}_3$); ^{13}C-NMR ($CDCl_3$-DMSO-d_6, δ, ppm): 164.70 (oxime $\underline{C}$=NOH), 163.60 ($\underline{C}$H=N), 160.10 (phenolic $\underline{C}$-OH), 155.51-112.54 (aromatic $\underline{C}$), 21.80 ($\underline{C}H_3$).

General synthesis of metal complexes, **M(L)$_2$**

A sample of the ligand (1.00 mmole) was dissolved in absolute ethanol (20 mL) by heating and left in a reaction flask. A solution of $M(AcO)_2$. nH_2O (0.50 mmole) in 10 mL absolute ethanol was added dropwise to the ligand solution with continuous stirring for 13 h at 50 ^{0}C under reflux. The precipitated complex was filtered off after overnight, washed with hot H_2O, cold EtOH and cold Et_2O several times and dried in vacuo.

Synthesis of bis (p-aminoacetophenonoxime 3,5-dicloroallysisilaldiminato) cobalt(**II**)

$Co(L)_2$ metal complex as carried out according to the general synthesis method of the given metal complexes.

IR spectrum (υ, cm^{-1}): 3315 (oxime O-H), 1609 (phenolic C=N), 1595 (oxime C=N), 1295 (C-O), 1007 (N-O).

Synthesis of bis (p-aminoacetophenonoxime 3,5-dicloroallysisilaldiminato) nickel(**II**)

$Ni(L)_2$ metal complex was carried out according to the general synthesis method of the given metal complexes.

IR spectrum (υ, cm^{-1}): 3335 (oxime O-H), 1613 (phenolic C=N), 1600 (oxime C=N), 1324 (C-O), 1007 (N-O).

Synthesis of bis (p-aminoacetophenonoxime 3,5-dicloroallysisilaldiminato) copper(**II**)

$Cu(L)_2$ metal complex was carried out according to the general synthesis method of the given metal complexes.

IR spectrum (υ, cm^{-1}): 3327 (oxime O-H), 1612 (phenolic C=N), 1599 (oxime C=N), 1310 (C-O), 1007 (N-O).

Synthesis of bis (p-aminoacetophenonoxime 3,5-dicloroallysisilaldiminato) zinc(**II**)

$Zn(L)_2$ metal complex was carried out according to the general synthesis method of the given metal complexes.

IR spectrum (υ, cm^{-1}): 3308 (oxime O-H), 1608 (phenolic C=N), 1597 (oxime C=N), 1296 (C-O), 1007 (N-O); ^{1}H-NMR ($CDCl_3$-DMSO-d_6, δ, ppm): 10.77 (s, 2H, oxime O$\underline{H}$), 8.56 (s, 2H, azomethine C$\underline{H}$=N), 7.71-6.86 (m, 12 H aromatic $\underline{H}$), 1.96 (s, 6H, C$\underline{H}_3$); ^{13}C-NMR ($CDCl_3$-DMSO-d_6, δ, ppm): 164.70 (oxime $\underline{C}$=NOH), 165.95 ($\underline{C}$H=N), 163.85 (phenolic $\underline{C}$-OH), 156.10-112.56 (aromatic $\underline{C}$), 21.82 ($\underline{C}H_3$).

Computational details

The structural and spectroscopic properties of (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime) have been investigated using density functional theory (DFT) [9] at the B3LYP level. The 6-311G (d, p) basis set has been used in the calculations. All the calculations have been carried out by using the GAUSSIAN09 program package [10]. Various spin multiplicities were investigated and it has been found that (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime) have spin singlet as the most stable (minimum total energy). The structure are taken as the local minima on potential energy surface having positive vibration frequencies. After geometric optimization with a tight and ultrafine integration, the electronic properties such as HOMO and LUMO energies were calculated using TD-DFT/6-311-G (d, p) to interpret the activity of the compounds. Hence, we used TD-DFT to obtain maximum wavelengths and compared with the experimental IR, and UV absorption of (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime). Optimized ground state structure of (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime) with atom numbering calculated by B3LYP/6-311-G (d,p) is given in Fig 1.

Results and Discussion

In the first part of this section, we will discuss the DFT simulation results to understand the spectral properties of (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime). For this purpose, we have present some results such as IR, Uv-Vis spectra, excess charge on atoms, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, the frontier molecular orbital energy gap (HOMO–LUMO difference in energy which is important to clarify the band gap energy to interpret the reactivity of the molecule), charge density (CD) of the studied molecule. In the second part, we have compared the some DFT results with experimental results obtained from this work.

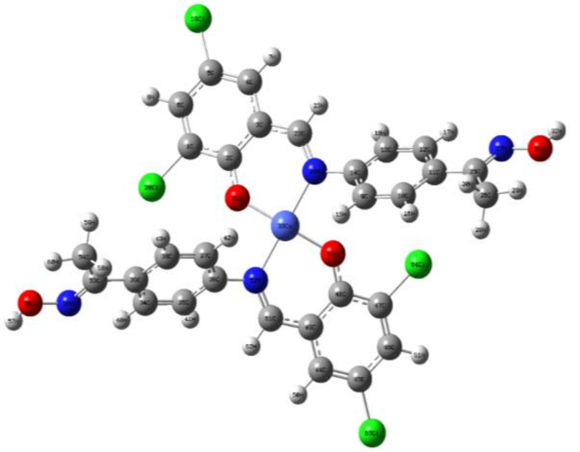


Fig. 1: Optimized grounds state geometry of Co(II) complexes.

Frontier molecular orbitals

Frontier molecular orbitals of a molecule such as HOMO and LUMO helps in understanding many properties of a compound like optical and electronic properties, stability, chemical hardness and softness reactivity etc.. The energy gap between HOMO and LUMO, known as gap of energy, is an important parameter to determine the electrical transport properties of a compound. In our investigation we found that (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime) compound has a total of 178 alpha and 177 beta orbitals. The energies of these orbitals are found to be -0.41746 (HOMO) eV and -0.40449 (LUMO) eV. The HOMO–LUMO plots for title compound is given in Fig 2 and the band gap is found to be 0.01297 electron volts. From the results of these plots we found that the maximum concentration of the frontier orbitals is on the rings of (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime). Since the (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime) compound has a very low band gap of around 0.013 eV which shows that it has low kinetic stability and high chemical reactivity.

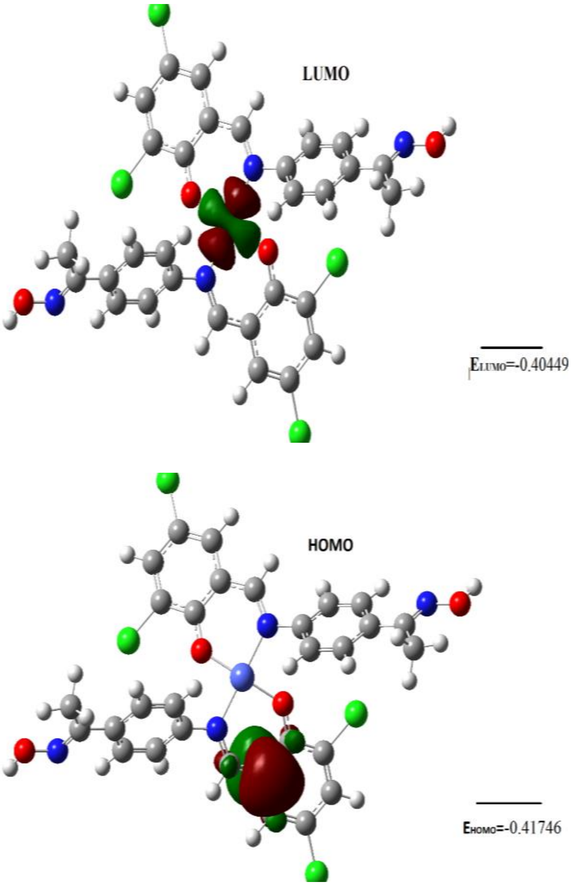


Fig. 2: Molecular orbitals of (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime).

Mulliken atomic charge and dipole moment

The Mulliken atomic charges display an important role in the application of quantum mechanical calculations. The Mulliken charges of (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime) compound were gathered in Table 1. The charges of the atoms in the different positions show different charge with each other for some carbon atoms. For example, the Mulliken charge of Carbon atom is mostly negative in (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime) compound. The Co atom exhibits a positive charge the value of Mulliken atomic charge is bigger than others. Hydrogen atom exhibits a positive charge because it is an acceptor atom.

The dipole moments are other important electronic properties. The bigger the dipole moment represents the stronger intermolecular interaction. The values of the components of dipole moments are X= -

0.0008 Y= -0.0008 Z= 5.2493 in the unit of Debye. The corresponding total dipole moment has been calculated to be 5.2493 Debye.

Table-1: Mulliken atomic charges of (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime) and spin densities.

Atom	charge	spin density
1 C	-0.417209	0.074343
2 C	0.559994	-0.042430
3 C	-0.107878	0.056665
4 C	0.032534	-0.023335
5 C	-0.364447	0.080641
6 C	0.132871	-0.059145
7 H	0.232130	0.000639
8 H	0.254639	0.002104
9 C	-0.116264	0.006038
10 C	-0.125241	-0.010188
11 C	-0.073377	-0.058528
12 C	-0.083077	-0.047714
13 C	-0.110134	0.033265
14 C	0.292569	-0.093809
15 H	0.158042	-0.000300
16 H	0.203870	0.000853
17 H	0.218723	0.002537
18 H	0.209975	-0.000943
19 Cl	0.122546	0.019539
20 Cl	0.093003	0.010699
21 O	-0.652057	0.111700
22 C	0.118945	-0.033742
23 H	0.248345	-0.000790
24 N	-0.773321	0.001431
25 C	0.237701	0.008147
26 C	-0.607494	-0.001845
27 N	-0.091427	-0.144520
28 H	0.232924	-0.000478
29 H	0.266076	0.000355
30 H	0.235029	-0.000565
31 O	-0.429463	-0.114264
32 H	0.431038	0.004678
33 Co	1.340873	1.438155
34 C	-0.083073	-0.047717
35 C	-0.110142	0.033258
36 C	0.292515	-0.093833
37 C	-0.116203	0.006030
38 C	-0.125239	-0.010174
39 C	-0.073385	-0.058565
40 H	0.218724	0.002537
41 H	0.209974	-0.000943
42 H	0.158045	-0.000300
43 H	0.203871	0.000853
44 C	0.032528	-0.023261
45 C	-0.364445	0.080567
46 C	0.132871	-0.059100
47 C	-0.417227	0.074313
48 C	0.560029	-0.042441
49 C	-0.107867	0.056592
50 H	0.232129	0.000637
51 H	0.254638	0.002102
52 N	-0.773322	0.001357
53 C	0.237705	0.008156
54 C	-0.607494	-0.001846
55 N	-0.091426	-0.144563
56 O	-0.429458	-0.114289
57 H	0.431041	0.004679
58 H	0.235032	-0.000565
59 H	0.232928	-0.000477
60 H	0.266076	0.000355
61 C	0.118930	-0.033628
62 H	0.248343	-0.000798
63 O	-0.652082	0.111658
64 Cl	0.093006	0.010695
65 Cl	0.122537	0.019521

Sum of Mulliken charges = 2.00000 spin density=1.00000

Vibrational analysis

The molecular vibrations of the (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime) compound were investigated by means of FT-IR spectroscopy (Fig 3). The computed vibrational spectra for the (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime) compound is given in Fig 4.

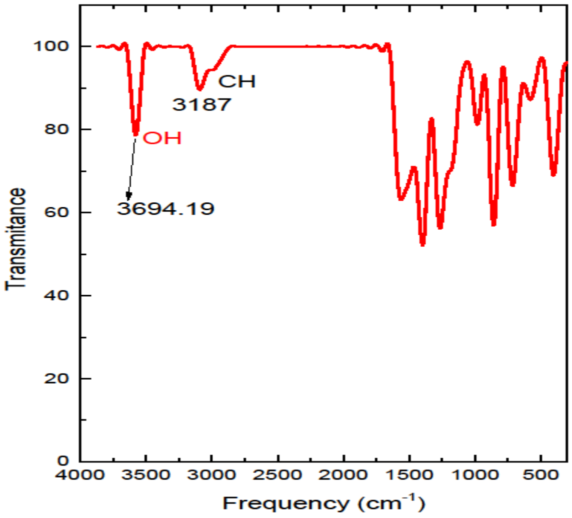


Fig. 3: Theoretical IR spectra of (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime).

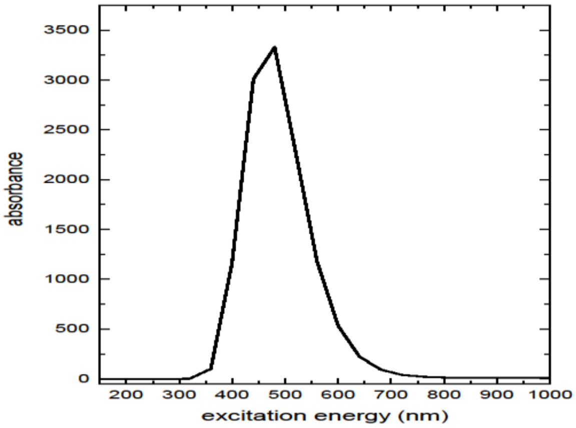
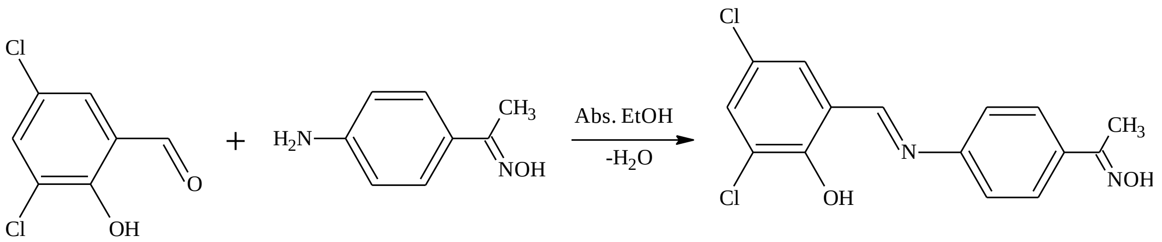


Fig. 4: Theoretical UV spectra of (3,5-dichlorosalicyliden-*p*-iminoacetophenone oxime).

Ligand (LH) was prepared by reaction of 3,5-dichlorosalicylaldehyde with *p*-aminoacetophenonoxime in absolute ethanol (scheme 1).



Scheme-1: Structure of the ligand.

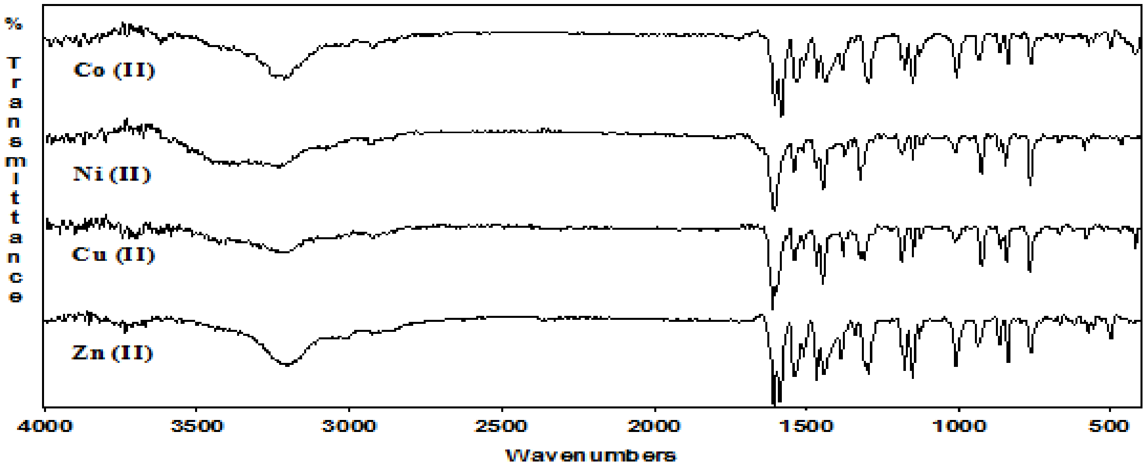


Fig. 5: Experimental IR spectrum of the complexes.

The general equations for the formation of synthesized metal complexes are given below:

$2LH+Co(CH_3COO)_2\bullet 4H_2O \rightarrow Co(L)_2+2CH_3COOH+4H_2O$
$2LH+Ni(CH_3COO)_2\bullet 4H_2O \rightarrow Ni(L)_2+2CH_3COOH+4H_2O$
$2LH + Cu(CH_3COO)_2\bullet H_2O \rightarrow Cu(L)_2+2CH_3COOH+H_2O$
$2LH+Zn(CH_3COO)_2\bullet 2H_2O \rightarrow Zn(L)_2+2CH_3COOH+2H_2O$

The analytical data confirm the proposed general molecular formula.

Infrared Spectra

The infrared spectrum of LH shows bands at *ca.* 3394, 3238, 1623, 1597, 1273 and 1004 cm^{-1}, assigned to O-H (oxime) [11-13]. O-H (phenolic), C=N (azomethine), C=N (oxime) [14-16], C-O and N-O, respectively. The infrared values obtained are consistent with those found for similar compounds and are listed in the experimental section. [17-18]. As can be seen from the theoretical IR calculations the OH and CH stretching picks are in 3694 cm-1 and 3187 cm-1 respectively. In the experimental results for Co complex the stretching band is very close to the theoretical one which is about 3100 cm-1. In the low wavenumber both theoretical and experimental results shown many structure which are corresponds to the vibrational mode of the complex. The absorption band corresponding to the aldehyde-related phenolic O-H in the IR spectra of the ligand is not observed in all metal complexes after complexation. The tension vibration at 1623 cm^{-1}, a characteristic of the group of azomethine (C=N), was observed as a strong band in the free ligand [19]. The coordination of the Schiff base with the azomethine nitrogen atom to the cobalt, nickel, copper and zinc ions is expected to reduce the electron density at the azomethine linkage thereby lowering the (C = N) absorption frequency. This band passes to the lower frequency 1608-1613 cm^{-1} due to the formation of metal chelates with metal ions of azomethine nitrogen. For this reason, this band changes to 1608-1613 cm^{-1} at low frequency after complexation and azomethine nitrogen [20] shows the coordination of cobalt, nickel, copper and zinc. The band observed at medium density at 3238 cm^{-1} in the (O-H) IR spectrum of the free ligand is not present in all the metal complexes obtained. This shows us the deprotonation of the Schiff base through oxygen atoms before coordination [21,22]. In addition, the C-O phenolic absorption frequency was observed at 1273 cm^{-1} in the ligand while it increased to 1295-1324 cm^{-1} in metal complexes. This shows us that another coordination is through phenolic oxygen [23]. The oxygen and nitrogen atoms of the oxime group were not coordinated to the metal atoms and the bands 3394 cm^{-1} and (O-H) 1597 cm^{-1} in the IR spectrum (C=N) remained almost unchanged. In the IR spectra of complex compounds, the (O-H), (C-N) and (N-O) stretching vibrations of the oxime group were not exposed to any chemical shifts because the oxime group N and O did not form a coordinative bond with the metal ions. This result shows that oximine nitrogen and oxygen atoms have no role in the coordination of metal ions.

NMR spectra

NMR spectra of Schiff base and diamagnetic Zn^{+2} complex were recorded using CDCl3/DMSO-d6 as solvent and the results obtained are detailed in the experimental section. Schiff base exhibits signals due to all expected proton in the expected region, and the integral ratios are in agreement with the number of proton in the structure and the literature [18].

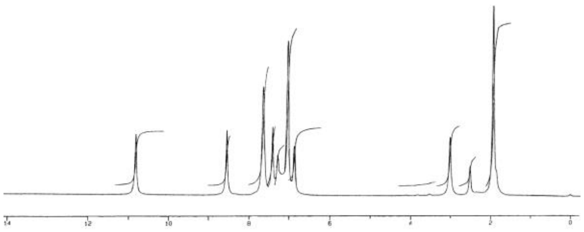


Fig. 6: ^{1}H-NMR spectrum of the Zn (II) complex.

Characteristic ^{1}H-NMR peaks are at 13.09 (phenolic OH), 10.75 (oxime OH), 8.62 (azomethine CH=N), 6.85-7.64 (Arom-H) and 1.95 ppm (CH_3). The phenolic OH signal, which had acidic proton at 13.09 ppm, disappeared with D_2O in the solution. The peak of the O-H group observed in the ligand in the ^{1}H-NMR spectrum of the Zn(II) complex is not observed. The peak of the O-H group observed in the ligand in the ^{1}H-NMR spectrum due to the formation of the Zn(II) complex was not observed. The peak of the azomethine proton of the ligand shifted up to 0.06 ppm due to the complex formation. These indicate that the ligand is coordinating with the metal through the nitrogen atom in the imine group and the phenolic C-O oxygen in the aldehyde group [24-26]. The data obtained in the ^{13}C-NMR spectrum gives detailed information on the structure of the ligand. CH = N and C-OH carbon atoms were observed at Schiff base at 163.60 and 160.10 ppm, respectively. The carbon atoms CH = N and C-OH in the ^{13}C-NMR spectrum of the Zn^{+2} complex were observed at 165.95 and 163.85 ppm, respectively. Slips corresponding to all carbons were observed to be compatible with the literature for the expected complex as well as the free ligand. The chemical shift values of the carbons of the other groups were observed at almost the same places as the ligand.

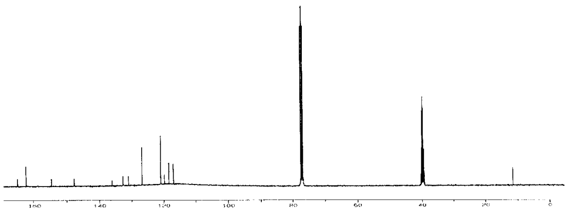


Fig. 7: ^{13}C-NMR spectrum of the Zn (II) complex.

Elemental analysis and magnetic moment

The analytical and physical properties of the complexes and the Schiff base are shown in Table 2. According to the results of the element analysis, it shows that the ligand forms products with a metal/ligand ratio of 1:2 with the metal salts and is consistent with the calculated values. The elemental analysis confirmed the compositions of the above synthesized compounds.

Magnetic susceptibility measurements of the complexes were taken at room temperature and are given in Table 2. Observed magnetic moment value of Co(II) complex was 4.04 BM and these results supports tetrahedral geometry for Co(II) complexes [27]. Magnetic moment value obtained was 2.88 BM, which is agreeable with the tetrahedral geometry for Ni(II) ion [28]. Obtained magnetic moment value for Cu(II) complex was 1.80 BM, further the value support the electronic spectral result [29]. The Zn^{+2} complex was found to be diamagnetic as expected.

UV-Vis

Electronic spectra of all synthesized compounds were recorded in DMF solution at room temperature. Electronic spectrum data of Schiff base and all metal complexes are given in the experimental section. The aromatic band of the ligand at 276 nm is attributed to benzene $\pi\rightarrow\pi^*$ transition. The band around 394 nm is due to the $n\rightarrow\pi^*$ transition of the non-bonding electrons present on nitrogen of the azomethine group in the Schiff base. The complexes of Co^{+2}, Ni^{+2} and Cu^{+2} show less intense shoulders at *ca.* 555-665 nm (ε = 151-196 L mol^{-1} cm^{-1}), which are assigned as *d-d* transition of the metal ions. The former band is probably due to the $^{4}A_2\rightarrow{}^{4}T_1$ (P) for Co^{+2}, $^{3}A_2\rightarrow{}^{3}T_2$ (F) for Ni^{+2} and $^{2}T_2\rightarrow{}^{2}E$ (G) for Cu^{+2} transition of tetrahedral geometry. All the complexes show an intense band at *ca* 375-390 nm which is assigned to $n\rightarrow\pi^*$ transition associated with azomethine linkage. The spectra of all the complexes show intense band at *ca* 430-445 nm (ε = 1.52-3.93 X 10^{3} L mol^{-1} cm$^{''1}$), which can be assigned to charge transfer transition of tetrahedral geometry [30-32].

Table-2: Analytical and physical data of the ligand and the complexes

Compounds	Formula	F.W(g/mol)	Color	Yield(%)	μ_{eff}(B.M.)	Elemental analysisCalculated (found) (%)		
						C	H	N
LH	$C_{15}H_{12}Cl_2N_2O_2$	323.17	yellow	74	—	55.75 (56.11)	3.74 (4.09)	8.67 (9.06)
Co(L)₂	$CoC_{30}H_{22}Cl_4N_4O_4$	703.27	light red	65	4.04	51.24 (50.88)	3.15 (2.79)	7.97 (8.37)
Ni(L)₂	$NiC_{30}H_{22}Cl_4N_4O_4$	703.03	light green	61	2.88	51.25 (50.90)	3.15 (2.76)	8.35 (7.96)
Cu(L)₂	$CuC_{30}H_{22}Cl_4N_4O_4$	707.88	light brown	59	1.80	50.90 (51.12)	3.13 (2.73)	7.91 (8.30)
Zn(L)₂	$ZnC_{30}H_{22}Cl_4N_4O_4$	709.74	light yellow	67	dia	50.77 (51.15)	3.12 (2.72)	7.89 (8.27)

Thermal studies

Thermogravimetric (TG) curves were recorded as a result of combustion of the synthesized complex compounds in the N_2 atmosphere at 20-800 ºC with an increase of 10 ºC per minute. Approximately 10 mg samples of the complexes were used in each case. When the TGA spectra of all of the complexes are examined, it has been observed that the thermal decomposition of the complexes takes place in two steps. It is also known that thermal stability affects the atomic radius of the metal atom and the thermal stability of electronegativity. [33]. TG spectra were taken to help characterize the complexes and to monitor the thermal stability of the compounds. In the complexes there is no weight loss up to 210 °C, indicating that the complexes are not water. It is believed that the TG curves of all complexes belong to the metal fractions and metal oxides of the mass losses below 715°C. [34-35]. The thermal stability of all complexes increases in the order: Cu < Zn < Ni < Co.

Conclusion

In this work, primarily oximes and their new Schiff base ligand were synthesized. The new Schiff base, derived from oxime, was used to complex with metal salts. Structures of Schiff's ligand and Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} metal complexes were characterized by elemental analyzes, Uv spectra, IR, ^{1}H and ^{13}C NMR spectra, thermogravimetric analyzes (TGA) and magnetic susceptibility measurements. According to TGA, IR and elemental analysis results, water molecules are not found in complexes. The equilibrium geometry, process of optimization geometry, density of state, charge density, dipole moment, IR densities are calculated by density functional theory method. HOMO-LUMO energies and Uv-Vis spectrum have calculated using time dependent density functional theory approach, basing on the optimized structure. All complexes obtained are mononuclear and tetrahedral. As a result, a new ligand not found in the literature and four complexes of this ligand were isolated. For these complexes, additional analytical and physical data are given in Table 2. It will be the basis for wider and longer-term research that has the potential to be applied according to the concrete data of the compounds obtained.

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References

1. H. I. Ugras, I. Basaran, T. Kilic, U. Cakir, Synthesis, complexation and antifungal, antibacterial activity studies of a new macrocyclic schiff base. *J. Het. Chem.*, **43,** 1679 (2006).
2. K.A. Dilmaghani, N.H. Jazani, A. Behrouz, F.M. Fakhraee, Synthesis, characterization and antibacterial activity of some schiff bases derived from 4-aminobenzoic acid, *Asian J. Chem*., **21,** 5947 (2009).
3. M.J. Hearn, M.H. Cynamon, M.F. Chen, R. Coppins, J. Davis, H.J-On Kang, A. Noble, B. Tu-Sekine, M.S. Terrot, D. Trombino, M. Thai, E.R. Webster, R. Wilson, Preparation and antitubercular activities in vitro and in vivo of novel schiff bases of isoniazid. *Eur. J. Med. Chem*., **44,** 4169 (2009).
4. L. Shi, M. Ge Hui, Shu-H. Tan, Qiu. Li Huan-, Yong-C. Song, Hai-L. Zhu, Synthesis and antimicrobial activities of Schiff bases derived from 5-chloro-salicylaldehyde, *Eur. J. Med. Chem*., **42,** 558 (2007).
5. L.A. Saghatforoush, F. Chalabian, A. Aminkhani, G. Karimnezhad, S. Ershad

Synthesis, spectroscopic characterization and antibacterial activity of new cobalt(II) complexes of unsymmetrical tetradentate (OSN_2) schiff base ligands, *Eur. Med. Chem*., **44,** 4490 (2009).

6. M.R. Yaftian, S. Rayati, R. Safarbali, N. Torabi, H.R. Khavasi, A new tetradentate N_2O_2-type Schiff base ligand. Synthesis, extractive properties towards transition metal ions and X-ray crystal structure of its nickel complex. *Trans. Met. Chem*., **32,** 374 (2007).
7. S. Salehzadeh, R. Golbedaghi, H.R. Khavasi, Synthesis, characterization, and crystal structure of a Ni(II) complex of an acyclic pentadentate schiff base; an agreement between the experimental and theoretical results. *J. Coord. Chem*., **62,** 2532 (2009).
8. Chen-X. Zhang, C. Cui, M. Lu, L.Yu, Yue-X. Zhan, In situ synthesis, characterization and crystal structure of a novel cobalt(III) complex with tridentate schiff base. *Synth React.. Inorg. Met-Org. Nano-Met. Chem.,* **39**, 136 (2009).
9. W. Kohn, L.J. Sham, *Phys. Rev*., **140,** 1133 (1965).
10. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, Gaussian 09, Revision B.01; Gaussian, Inc., Wallingford CT. (2009).
11. R. Ramesh, M. Sivagamasundari, Synthesis, spectral and antifungal activity of Ru(II) mixed ‑ ligand complexes. *Synth. React. Inorg. Met-Org. Nano-Met. Chem.,* **33,** 899 (2003).
12. S. Tuna, E. Canpolat, M. Kaya, Synthesis and characterization of a new 4-methoxysalicyliden-*p*-aminoacetophenoneoxime and its complexes with Co(II), Ni(II), Cu(II) and Zn(II). *Polish. J. Chem*., **80,** 1651 (2006).
13. E. Canpolat, H. Şahal, M. Kaya, S. Gür, Synthesis, characterization antibacterial and antifungal activities studies of copper(II), cobalt(II) and zinc(II) complexes of the schiff base ligand derived from 4,4-diaminodiphenylether. *J. Chem. Soc. Pakistan.,* **36,** 106 (2014).

A. Saxena, J.P. Tandon, Structural features of some organotin(IV) complexes of semi-and thio-semicarbazones. *Polyhedron*, **3**, 681 (1984).

14. Y.N. Kukushkin, V.K. Krylov, S.F. Kaplan, M. Calligaris, E. Zangrando, A.J.L. Pombeiro, V.Y. Kukushkin Different chlorination modes of oximes: chlorination of salicylaldoxime coordinated to platinum**.** *Inorg. Chim. Acta*., **285,** 116 (1999).
15. E.G. Bakırdere, E. Canpolat, M. Kaya, N. Gür, Synthesis, antibacterial and antifungal activity of a new 2-{(e)-[(4-aminophenyl) ımino]methyl}-6-methoxy-4-nitrophenol and its complexes with Co(II), Ni(II), Cu(II) and Zn(II). *J. Chem. Soc. Pakistan.,* **34,** 1186 (2012).
16. S, Satapathy, B. Sahoo, Salicylaldazinate metal chelates and their I.R. spectra. *J. lnorg. Nucl. Chem*., **32,** 2223 (1970).
17. E. Canpolat, Studies on mononuclear chelates derived from substituted schiff bases ligands (part 8): synthesis and characterization of a new 5-chlorosalicyliden-*p*-aminoacetophenoneoxime and its complexes with Co(II), Ni(II), Cu(II) and Zn(II), Polish. J. Chem., **79,** 619 (2005).
18. B. Khera, A.K. Sharma, N.K. Kaushik, Bis(indenyl)titanium(IV) and zirconium(IV) complexes of monofunctional bidentate salicylidimines. *Polyhedron*, **2,** 1177 (1983).
19. R.C. Maurya, P. Patel, S. Rajput, Synthesis and characterization of n ‑ (*o* ‑ vanillinidene) ‑ *p* ‑ anisidine and N,N′ ‑ *bis*(*o* ‑ vanillinidene)ethylenediamine and their metal complexes, *Synth React Inorg Met-Org. Nano-Met. Chem.*, **33,** 817 (2003).
20. P. Bamfield, The reaction of cobalt halides with *N*-arylsalicylideneimines. *J. Chem. Soc. A: Inorg. Phy.s Theor.*, 804 (1967).
21. E. Canpolat, M. Kaya, Studies on mononuclear chelates derived from substituted schiff bases ligands: synthesis and characterization of a new 5-methoxysalicyliden-*p*-aminoacetophenoneoxime and its complexes with Co(II), Ni(II), Cu(II) and Zn(II), *Russian J. Coord. Chem.* **31**, 790 (2005).
22. L.J. Boucher, Manganese schiff's base complexes—II: Synthesis and spectroscopy of chloro-complexes of some derivatives of (salicylaldehydeethylenediimato) manganese(III). *J. lnorg. Nucl. Chem.,* **36,** 531 (1974).
23. E.M. Nour, A.A. Taha, I.S. Alnaimi, Infrared and Raman studies of $[UO_2(salen)(L)]$ ($L=H_2O$ and CH_3OH), Inorg. Chem. Acta., **141**, 139 (1988).
24. B.V. Agarwala, S. Hingorani, V. Puri, C.L. Khetrapal, G.A. Naganagowda, Physicochemical studies of (*o*-vanillin thiosemicarbazonato)-nickel(II) chelate. *Trans. Met. Chem.*, **19,** 25 (1994).
25. E. Canpolat, A. Yazıcı, M. Kaya, Studies on mononuclear chelates derived from substituted schiff-base ligands (part 10): synthesis and characterization of a new 4-hydroxysalicyliden-*p*-aminoacetophenoneoxime and its complexes with Co(II) Ni(II), Cu(II) and Zn(II), *J. Coord. Chem.,* **60**, 473 (2007).

26. P.K. Panda, S.B. Mishra, B.K. Mohapatra, Complexes of cobalt(II), nickel(II), copper(II) and zinc(II) with dicyanadiamide. *J. lnorg. Nucl. Chem.*, **42,** 497 (1980).
27. D.X. West, A.A. Nassar, F.A. El-Saied, M.I. Ayad, Copper(II) complexes of 2-aminoacetophenone N(4)-substituted thiosemicarbazones. Trans. Met. Chem., **23,** 321 (1998).
28. M.M. Aboaly, M.M.H. Khalil, Synthesis and spectroscopic study of Cu(II), Ni(II), and Co(II) complexes of the ligand salicylidene-2-amino thiophenol. *Spectr. Lett*., **34,** 495 (2001).
29. S. Yamada, A. Takeuchi, The conformation and interconversion of schiff base complexes of nickel(II) and copper(II), *Coord. Chem. Rev.,* **43,** 187 (1982).
30. M.R. Wagner, F.A. Walker, Spectroscopic study of 1:1 copper(II) complexes with schiff base ligands derived from salicylaldehyde and L-histidine and its analogs, *Inorg. Chem.,* **22,** 3021 (1983).
31. R. Atkins, G. Brewer, E. Kokot, G.M. Mockler, E. Sinn, Copper(II) and nickel(II) complexes of unsymmetrical tetradentate schiff base ligands, *Inorg. Chem.,* **24,** 127 (1985).
32. W. Brzyska, A. Krol, Properties and thermal decomposition in air atmosphere of Co(II), Ni(II), Cu(II) and Zn(II) benzene-1,2-dioxyacetates. *Therm. Acta.,* **223,** 241 (1993).
33. S-Lan. Li, D-Xin. Liu, S-Qiang. Zhang, H. Wang, Z-He. Yang, Determination of mechanism functions and kinetic parameters of thermodecomposition of complexes with the schiff base derived from 3-methoxysalicylaldehyde and diamine with non-isothermal TG and DTG curves. *Therm. Acta.*, **275**, 215 (1996).
34. A.A. El-Bindary, A.Z. El-Sonbati Synthesis and properties of complexes of copper(II), nickel(II), cobalt(II) and uranyl ions with 3-(*p*-tolylsulphonamido)rhodanine. *Polish. J. Chem.*, **74,** 615 (2000).