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

 ¹Ali Çapan*, ²Erdal Canpolat, ³Henar Sleman and ³Niyazi Bulut
 ¹Vocational School of Higher Education in Nizip, Department of Food Technology, Gaziantep University, Turkey.
 ²Faculty of Education, Department of Elementary Science Education, Firat` University, 23119,Elaziğ, Turkey,
 ³ Firat University Faculty of Science Physics Department, 23119 Elazig, Turkey. capan027@gmail.com*

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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, ¹H-NMR, ¹³C-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 3.5dichlorosalicylidene-p-iminoacetophenone oxime (LH) Metal complexes have been reported to have a tetracoordinated build-up tendency in the general comparison d⁷, d⁸, d⁹ and d¹⁰ configurations. The Schiff

base ligand synthesized in this work is given in Scheme 1. All compounds were characterized by IR, ¹H-NMR, ¹³C-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 ¹H and ¹³C-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 paminoacetophenone oxime. 3,5-Dicloxalisilaldehyde was used in the synthesis of the Schiff base. [M(AcO)₂.nH₂O] 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

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 CHCl₃. 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 (v, cm⁻¹): 3394 (oxime O-H), 3238 (phenolic O-H), 1623 (phenolic C=N), 1597 (oxime C=N), 1273 (C-O), 1004 (N-O); ¹H-NMR (CDCl₃-DMSO- d_6 , δ , ppm): 13.09 (s, 1H, phenolic O<u>H</u>), 10.75 (s, 1H, oxime O<u>H</u>), 8.62 (s, 1H, azomethine C<u>H</u>=N), 7.64-6.85 (m, 6H aromatic <u>H</u>), 1.95 (s, 3H, C<u>H</u>₃); ¹³C-NMR (CDCl₃-DMSO- d_6 , δ , ppm): 164.70 (oxime <u>C</u>=NOH), 163.60 (<u>C</u>H=N), 160.10 (phenolic <u>C</u>-OH), 155.51-112.54 (aromatic <u>C</u>), 21.80 (<u>C</u>H₃).

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 $M(AcO)_2$. nH₂O (0.50 mmole) in 10 mL absolute ethanol was added dropwise to the ligand solution with continuous stirring for 13 h at 50 °C under reflux. The precipitated complex was filtered off after overnight, washed with hot H₂O, cold EtOH and cold Et₂O several times and dried in vacuo.

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

Co(L)₂ metal complex as carried out according to the general synthesis method of the given metal complexes.

IR spectrum (v, 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 3,5dicloroallysisilaldiminato) nickel(**II**)

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

IR spectrum (u, 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 3,5dicloroallysisilaldiminato) copper(**II**)

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

IR spectrum (v, 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 3,5dicloroallysisilaldiminato) zinc(***II**)

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

IR spectrum (v, cm⁻¹): 3308 (oxime O-H), 1608 (phenolic C=N), 1597 (oxime C=N), 1296 (C-O), 1007 (N-O); ¹H-NMR (CDCl₃-DMSO- d_6 , δ , ppm): 10.77 (s, 2H, oxime O<u>H</u>), 8.56 (s, 2H, azomethine C<u>H</u>=N), 7.71-6.86 (m, 12 H aromatic <u>H</u>), 1.96 (s, 6H, C<u>H</u>₃); ¹³C-NMR (CDCl₃-DMSO- d_6 , δ , ppm): 164.70 (oxime <u>C</u>=NOH), 165.95 (<u>C</u>H=N), 163.85 (phenolic <u>C</u>-OH), 156.10-112.56 (aromatic <u>C</u>), 21.82 (<u>C</u>H₃).

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 (3,5dichlorosalicyliden-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-piminoacetophenone oxime). Optimized ground state of (3,5-dichlorosalicyliden-pstructure 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-piminoacetophenone 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 (3,5dichlorosalicyliden-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 (3,5dichlorosalicyliden-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 (3,5-dichlorosalicyliden-p-iminoacetophenone in 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.

$ \begin{array}{c} 1 \ C \ -0.417209 \ 0.074343 \\ 2 \ C \ 0.55994 \ -0.042430 \\ 3 \ C \ -0.03787 \ 0.056665 \\ 4 \ C \ 0.032534 \ -0.023335 \\ 5 \ C \ -0.36447 \ 0.080641 \\ 6 \ C \ 0.132871 \ -0.059145 \\ 7 \ H \ 0.232130 \ 0.000638 \\ 10 \ C \ -0.116264 \ 0.006038 \\ 10 \ C \ -0.116264 \ 0.006038 \\ 10 \ C \ -0.116264 \ 0.006038 \\ 10 \ C \ -0.01737 \ -0.058528 \\ 12 \ C \ -0.083077 \ -0.047714 \\ 13 \ C \ -0.07377 \ -0.058528 \\ 12 \ C \ -0.083077 \ -0.047714 \\ 13 \ C \ -0.0110134 \ 0.033265 \\ 14 \ C \ 0.292569 \ -0.093809 \\ 15 \ H \ 0.218723 \ 0.000853 \\ 17 \ H \ 0.218723 \ 0.000853 \\ 17 \ H \ 0.218723 \ 0.0002537 \\ 18 \ H \ 0.203870 \ 0.000853 \\ 19 \ C \ 10.128723 \ 0.002537 \\ 18 \ H \ 0.203870 \ 0.000853 \\ 19 \ C \ 10.22546 \ 0.019539 \\ 20 \ C1 \ 0.093003 \ 0.01699 \\ 21 \ O \ -0.652057 \ 0.111700 \\ 22 \ C \ 0.118945 \ -0.03742 \\ 23 \ H \ 0.248345 \ -0.000790 \\ 24 \ N \ -0.77322 \ 0.0008147 \\ 26 \ C \ -0.067494 \ -0.001845 \\ 27 \ N \ -0.091427 \ -0.144520 \\ 28 \ H \ 0.232924 \ -0.000478 \\ 29 \ H \ 0.26076 \ 0.000355 \\ 30 \ H \ 0.235029 \ -0.000555 \\ 31 \ O \ -0.429463 \ -0.114264 \\ 32 \ H \ 0.431038 \ 0.004678 \\ 33 \ C \ 1.340873 \ 1.438155 \\ 34 \ C \ -0.08373 \ 1.438155 \\ 34 \ C \ -0.08373 \ 1.438155 \\ 34 \ C \ -0.08373 \ 1.438155 \\ 34 \ C \ -0.016373 \ 1.438155 \\ 34 \ C \ -0.033258 \\ 36 \ C \ 0.292515 \ -0.093833 \\ 37 \ C \ -0.116203 \ 0.00633 \\ 38 \ C \ -0.116203 \ 0.00633 \\ 38 \ C \ -0.116203 \ 0.00633 \\ 38 \ C \ -0.025257 \\ 41 \ H \ 0.20974 \ -0.000943 \\ 42 \ H \ 0.23528 \ -0.033258 \\ 36 \ C \ 0.023258 \ -0.033258 \\ 36 \ C \ 0.032528 \ -0.033258 \\ 36 \ C \ 0.032528 \ -0.033256 \\ 50 \ H \ 0.23529 \ -0.000478 \\ 39 \ C \ -0.073385 \ -0.058565 \\ 40 \ H \ 0.218724 \ 0.002537 \\ 41 \ H \ 0.20974 \ -0.000853 \\ 44 \ C \ 0.032528 \ -0.003361 \\ 45 \ C \ -0.067494 \ -0.014456 \\ 55 \ N \ -0.091426 \ -0.144563 \\ 56 \ C \ -0.042948 \ -0.114269 \\ 57 \ H \ 0.226077 \ -0.06557 \\ 59 \ H \ 0.23520 \ -0.00355 \\ 50 \ H \ 0.23520 \ -0.00355 \\ 50 \ H \ 0.23520 \ -0.00355 \\ 50 \ H \ 0.235032 \ -0.00355 \\ 50 \ H \ 0.235032 \ -0.00355 \\ 50 \ H \ 0.2$	Atom charge	spin density
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$\begin{array}{c} 4 \ C \ 0.032534 \ -0.023335 \\ 5 \ C \ -0.364447 \ 0.080641 \\ 6 \ C \ 0.13251 \ -0.059145 \\ 7 \ H \ 0.232130 \ 0.000639 \\ 8 \ H \ 0.254639 \ 0.002104 \\ 9 \ C \ -0.116264 \ 0.006038 \\ 10 \ C \ -0.116264 \ 0.006038 \\ 11 \ C \ -0.073377 \ -0.058528 \\ 12 \ C \ -0.083077 \ -0.047714 \\ 13 \ C \ -0.010134 \ 0.033265 \\ 14 \ C \ 0.0292569 \ -0.093809 \\ 15 \ H \ 0.158042 \ -0.000300 \\ 16 \ H \ 0.20370 \ 0.000853 \\ 17 \ H \ 0.218723 \ 0.002537 \\ 18 \ H \ 0.20975 \ -0.000943 \\ 19 \ C1 \ 0.023870 \ 0.000943 \\ 19 \ C1 \ 0.023670 \ 0.000943 \\ 19 \ C1 \ 0.023670 \ 0.010699 \\ 21 \ O \ -0.652057 \ 0.111700 \\ 22 \ C \ 0.093003 \ 0.010699 \\ 21 \ O \ -0.652057 \ 0.111700 \\ 22 \ C \ 0.01845 \ -0.003742 \\ 23 \ H \ 0.24845 \ -0.00790 \\ 24 \ N \ -0.773321 \ 0.001431 \\ 25 \ C \ 0.0237711 \ 0.008147 \\ 26 \ C \ -0.06794 \ -0.001845 \\ 27 \ N \ -0.091427 \ -0.144520 \\ 28 \ H \ 0.232924 \ -0.000355 \\ 30 \ H \ 0.25029 \ -0.000355 \\ 31 \ O \ -0.429463 \ -0.01427 \\ 43 \ H \ 0.235029 \ -0.000555 \\ 31 \ O \ -0.429463 \ -0.01427 \\ 33 \ C0 \ -0.144274 \ -0.003373 \ -0.04678 \\ 33 \ C0 \ -0.1340873 \ 1.438155 \\ 34 \ C \ -0.06303 \ -0.0675 \\ 33 \ C \ -0.110142 \ 0.033258 \\ 36 \ C \ -0.023571 \\ 41 \ H \ 0.229215 \ -0.093833 \\ 377 \ C \ -0.110142 \ 0.033258 \\ 36 \ C \ -0.023571 \\ 41 \ H \ 0.203871 \ -0.008433 \\ 377 \ C \ -0.110142 \ 0.033258 \\ 36 \ C \ -0.023871 \ -0.008433 \\ 42 \ H \ 0.132871 \ -0.089100 \\ 43 \ H \ 0.23871 \ -0.008053 \\ 44 \ C \ -0.03385 \ -0.088565 \\ 40 \ H \ 0.218724 \ -0.002537 \\ 41 \ H \ 0.20871 \ -0.00853 \\ 44 \ C \ -0.033251 \ -0.008565 \\ 40 \ H \ 0.218724 \ -0.002537 \\ 41 \ H \ 0.20871 \ -0.00853 \\ 42 \ H \ 0.32871 \ -0.00853 \\ 44 \ C \ -0.033251 \ -0.00300 \\ 43 \ H \ 0.23871 \ -0.008567 \\ 55 \ N \ -0.023871 \ -0.00853 \\ 55 \ N \ -0.023871 \ -0.00853 \\ 55 \ N \ -0.023871 \ -0.00853 \\ 56 \ C \ -0.032871 \ -0.00853 \\ 56 \ C \ -0.032871 \ -0.00853 \\ 56 \ C \ -0.03288 \ -0.03268 \\ 56 \ N \ -0.03288 \ -0.03268 \\ 56 \ N \ -0.03484 \ -0.03484 \ -0.004679 \\ 58 \ H \ 0.23803 \ -0.00355 \\ 59 \ H \ 0.23803 \ -0.00355 \\ 50 \ H \ 0.23$	3 C -0.107878	0.056665
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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 C1 0.122546 0.019539 20 C1 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 0.235029 -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 -0.116120 3.006030 38 C -0.125239 -0.00174 39 C -0.073385 -0.058565 40 H 0.218724 0.002537 41 H 0.20871 0.008137 42 H 0.158045 -0.003383 37 C -0.116203 0.006030 38 C -0.125239 -0.01174 39 C -0.073385 -0.058565 40 H 0.218724 0.002537 41 H 0.20871 0.00853 44 C 0.032528 -0.0232161 45 C -0.034445 0.000300 43 H 0.23871 0.000853 44 C 0.032528 -0.023261 45 C -0.12445 0.000300 45 H 0.23871 0.00853 46 C 0.125239 -0.01174 39 C -0.073385 -0.058565 40 H 0.218724 0.002537 41 H 0.20974 -0.000943 42 H 0.158045 -0.000300 43 H 0.23871 -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 0.23483 -0.021825 50 H 0.232129 0.000637 51 H 0.23483 -0.021825 50 H 0.232129 0.000853 51 C -0.124538 -0.02326 51 H 0.23483 -0.002102 52 N -0.773322 0.001357 53 C 0.237705 0.008156 54 C -0.429458 -0.114289 57 H 0.431041 0.004679 58 H 0.235032 -0.004567 59 H 0.235032 -0.004567 50 H 0.235032 -0.004567 51 H 0.25483 0.002102 52 N -0.773322 0.001357 53 C 0.237705 0.008156 54 C -0.667084 -0.001384 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 0.232547 -0.02567 50 H 0.232547 -0.02567 50 H 0.232547 -0.02567 50 H 0.235032 -0.000565 50 H 0.235032 -0.000565 50 H 0.235032 -0.000565 50 H 0.235032 -0.000565 50 H 0.235032 -0.00056	5 C -0.364447	0.080641
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$ \begin{array}{c} 8 \ H \ 0.2254639 \ 0.002104 \\ 9 \ C \ -0.116264 \ 0.006038 \\ 10 \ C \ -0.073377 \ -0.058528 \\ 11 \ C \ -0.073377 \ -0.058528 \\ 12 \ C \ -0.083077 \ -0.047714 \\ 13 \ C \ -0.110134 \ 0.03265 \\ 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 \ C1 \ 0.122546 \ 0.019539 \\ 20 \ C1 \ 0.093003 \ 0.010699 \\ 21 \ O \ -0.652057 \ 0.111700 \\ 22 \ C \ 0.118945 \ -0.03742 \\ 23 \ H \ 0.248345 \ -0.000790 \\ 24 \ N \ -0.773321 \ 0.001845 \\ 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 \ 0.26076 \ 0.000355 \\ 30 \ H \ 0.235029 \ -0.000565 \\ 31 \ O \ -0.429463 \ -0.114264 \\ 32 \ H \ 0.235029 \ -0.0004678 \\ 33 \ Co \ 1.340873 \ 1.438155 \\ 34 \ C \ -0.083073 \ -0.047717 \\ 35 \ C \ 0.10142 \ 0.03258 \\ 36 \ C \ 0.292515 \ -0.093833 \\ 37 \ C \ -0.116203 \ 0.0006030 \\ 38 \ C \ 0.125239 \ -0.010174 \\ 39 \ C \ -0.073385 \ -0.058565 \\ 40 \ H \ 0.218724 \ 0.002537 \\ 41 \ H \ 0.20974 \ -0.000943 \\ 42 \ H \ 0.158045 \ -0.00300 \\ 43 \ H \ 0.20371 \ 0.000833 \\ 44 \ C \ 0.032528 \ -0.023261 \\ 45 \ C \ -0.364445 \ 0.080567 \\ 46 \ C \ 0.132871 \ -0.059100 \\ 47 \ C \ -0.47270 \ 0.773313 \\ 48 \ C \ 0.56029 \ -0.00437 \\ 41 \ H \ 0.20371 \ -0.059100 \\ 47 \ C \ -0.47270 \ 0.773313 \\ 48 \ C \ 0.56029 \ -0.004241 \\ 49 \ C \ -0.073313 \ -0.08556 \\ 50 \ H \ 0.232228 \ -0.000637 \\ 51 \ H \ 0.220271 \ -0.008156 \\ 54 \ C \ -0.073322 \ 0.000637 \\ 51 \ H \ 0.220270 \ -0.008156 \\ 54 \ C \ -0.073322 \ 0.000637 \\ 55 \ N \ -0.073322 \ 0.000657 \\ 59 \ H \ 0.232028 \ -0.000477 \\ 56 $	7 H 0.232130	0.000639
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 C1 0.122546 0.019539 20 C1 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 C 0.110142 0.033258 36 C 0.292515 -0.03833 37 C -0.116203 0.006030 38 C -0.125239 -0.010174 39 C -0.073385 -0.058565 40 H 0.215724 0.002537 41 H 0.209974 -0.000813 42 C -0.03871 0.000813 42 C -0.03871 0.000813 44 C 0.032528 -0.02361 45 C -0.364445 0.08067 46 C 0.132871 -0.000813 47 C -0.417227 0.073313 48 C 0.56029 -0.00365 50 H 0.23512 -0.00385 50 H 0.23512 -0.00385 51 H 0.23528 -0.03361 52 C 0.122519 -0.00385 53 C 0.112524 -0.003856 54 O H 0.215724 0.002537 53 C -0.110142 -0.03258 54 C 0.032528 -0.023261 45 C -0.364445 0.080657 46 C 0.132871 -0.009813 47 C -0.417227 0.074313 48 C 0.560029 -0.042441 49 C -0.107867 0.0559100 47 C -0.417227 0.074313 48 C 0.560029 -0.042441 49 C -0.107867 0.05592 50 H 0.232129 0.000637 51 H 0.232129 0.000637 51 H 0.232129 0.000637 51 H 0.23229 0.000637 51 H 0.23229 0.000477 53 C 0.237705 0.008156 54 C 0.013281 -0.003815 55 N -0.091426 -0.144563 56 C 0.142831 -0.14863 56 C 0.0142831 -0.01846 55 N -0.091426 -0.144563 56 C 0.0142329 0.000477 56 H 0.232129 0.000637 51 H 0.232129 0.000637 51 H 0.23229 0.000477 53 H 0.23229 0.000477 54 H 0.236032 0.00057 55 H 0.23229 0.000477 56 H 0.236032 0.01057 57 H 0.431041 0.004679 58 H 0.236032 0.01057 59 H 0.23229 0.000477 50 H 0.236032 0.00057 51 H 0.236032 0.00057 52 N -0.073322 0.00037 53 H 0.235032 0.00057 54 H 0.24683 0.111658 55 C 0.011658 56 C 0.0118531 56 C 0.014551 57 H 0.431041 0.004679 58 H 0.246374 0.0007	8 H 0.254639	0.002104
$\begin{array}{c} 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 & -0.000853\\ 17 \ H & 0.203870 & 0.000853\\ 17 \ H & 0.203870 & 0.000853\\ 17 \ H & 0.203870 & 0.000853\\ 19 \ C & 0.128723 & 0.002537\\ 18 \ H & 0.209975 & -0.000943\\ 19 \ C & 0.128723 & 0.002537\\ 18 \ H & 0.209975 & -0.000943\\ 19 \ C & 0.12845 & -0.03742\\ 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 & 0.232924 & -0.000478\\ 29 \ H & 0.266076 & 0.000355\\ 31 \ H & 0.232924 & -0.000478\\ 32 \ H & 0.431038 & 0.004678\\ 33 \ C & 1.340873 & 1.438155\\ 34 \ C & -0.083073 & -0.047717\\ 35 \ C & -0.116203 & 0.066030\\ 36 \ C & 0.292515 & -0.093833\\ 37 \ C & -0.116203 & 0.06030\\ 38 \ C & -0.125239 & -0.010174\\ 39 \ C & -0.073385 & -0.058565\\ 40 \ H & 0.218724 & 0.002537\\ 41 \ H & 0.20974 & -0.00943\\ 42 \ H & 0.23871 & 0.000853\\ 44 \ C & 0.032528 & -0.03261\\ 45 \ C & -0.364445 & 0.080567\\ 46 \ C & 0.132871 & -0.00943\\ 42 \ H & 0.23871 & 0.000853\\ 44 \ C & 0.032528 & -0.023261\\ 45 \ C & -0.073413\\ 48 \ C & 0.560029 & -0.042441\\ 49 \ C & -0.107867 & 0.056592\\ 50 \ H & 0.232129 & 0.000637\\ 51 \ H & 0.22458 & -0.114289\\ 57 \ H & 0.431041 & 0.004679\\ 58 \ H & 0.235022 & -0.00355\\ 59 \ H & 0.235022 & -0.00477\\ 60 \ H & 0.266076 & 0.00355\\ 59 \ H & 0.235022 & -0.00477\\ 60 \ H & 0.266076 & 0.00355\\ 50 \ H & 0.235022 & -0.00477\\ 60 \ H & 0.266076 & 0.00355\\ 50 \ H & 0.235022 & -0.00477\\ 50 \ H & 0.235022 & -0.00477\\ 50 \ H & 0.235032 & -0.00567\\ 50 \ H & 0.235032 & -0.00567\\ 50 \ H & 0.235032 & -0.000677\\ 51 \ H & 0.24633 & -0.003528\\ 52 \ N & -0.073322 & 0.000677\\ 53 \ H & 0.235032 & -0.00477\\ 56 \ H & 0.266076 & 0.00355\\ 57 \ H & 0.431041 & 0.004679\\ 58 \ H & 0.266076 & 0.00355\\ 59 \ H & 0.235032 & -0.00477\\ 50 \ H & 0.266076 & 0.00355\\ 50 \ H & 0.236282 & 0.111658\\ 61 \ C & 0.0730$	9 C -0.116264	0.006038
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 C1 $0.122546 - 0.019539$ 20 C1 $0.093003 - 0.010699$ 21 O $-0.652057 - 0.111700$ 22 C $0.118945 - 0.030742$ 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 $0.232024 - 0.000478$ 29 H $0.26076 - 0.000355$ 30 O $-0.429463 - 0.114264$ 32 H $0.243073 - 1.04873$ 34 C $-0.083073 - 0.047717$ 35 C $-0.110142 - 0.032388$ 36 C $0.292515 - 0.093833$ 37 C $-0.116203 - 0.00630$ 38 C $-0.125239 - 0.010174$ 39 C $-0.073385 - 0.058565$ 40 H $0.218724 - 0.002537$ 41 H $0.218724 - 0.002537$ 41 H $0.218724 - 0.002537$ 41 H $0.218714 - 0.002537$ 41 H $0.21871 - 0.000853$ 44 C $0.032583 - 0.023261$ 45 C $-0.364445 - 0.000300$ 43 H $0.203871 - 0.000853$ 44 C $0.032583 - 0.023261$ 45 C $-0.364445 - 0.000300$ 43 H $0.223219 - 0.000165$ 31 H $0.223219 - 0.0003657$ 31 H $0.223271 - 0.059100$ 47 C $-0.417227 - 0.074313$ 48 C $0.560029 - 0.042441$ 49 C $-0.17367 - 0.055920$ 50 H $0.232129 - 0.000157$ 51 H $0.223229 - 0.000157$ 52 N $-0.773322 - 0.001357$ 53 C $0.237705 - 0.008156$ 54 C $-0.474945 - 0.114283$ 55 N $-0.091426 - 0.144563$ 56 O $-0.429458 - 0.114289$ 57 H $0.431041 - 0.004679$ 58 H $0.232028 - 0.000477$ 60 H $0.266076 - 0.000355$ 59 H $0.23228 - 0.000477$ 60 H $0.266076 - 0.000355$ 50 H $0.23228 - 0.000477$ 51 H $0.23228 - 0.000477$ 51 H $0.232028 - 0.000477$ 52 N $-0.77322 - 0.001357$ 53 C $0.237705 - 0.008156$ 54 C $-0.674948 - 0.114289$ 57 H $0.431041 - 0.004679$ 58 H $0.235028 - 0.000477$ 50 H $0.23228 - 0.000477$ 50 H $0.23228 - 0.000477$ 51 H $0.236028 - 0.114658$ 52 O H $0.236076 - 0.003355$ 53 C D H $0.23228 - 0.000477$ 54 C 0.0733628 55 C $0.018930 - 0.033628$ 56 C $0.018930 - 0.033628$ 57 C $0.033068 - 0.016951$ 59 C $0.003066 - 0.$	10 C -0.125241	-0.010188
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 $0.20975 -0.000943$ 19 C1 $0.122546 0.019539$ 20 C1 $0.093003 0.010699$ 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 $0.232024 -0.000478$ 29 H $0.266076 0.000355$ 30 H $0.235029 -0.000676$ 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 $-0.125239 -0.00174$ 39 C $-0.073385 -0.058565$ 40 H $0.218724 0.002537$ 41 H $0.20974 -0.000301$ 42 N $-0.00301 -0.00174$ 43 C $-0.043271 -0.00301$ 43 H $0.203871 0.000853$ 44 C $0.032528 -0.023261$ 45 C $-0.34445 0.080567$ 46 C $0.132871 -0.059100$ 47 C $-0.417227 0.074313$ 48 C $0.56029 -0.042441$ 49 C $-0.107367 0.05592$ 50 H $0.232129 0.000637$ 51 H $0.23228 -0.000477$ 51 H $0.232028 -0.000798$ 52 O 0.00798 53 O $0.073320 0.000798$ 54 C $0.073342 0.011857$ 55 O 0.0033628 61 C $0.018930 -0.033628$ 62 C $0.003006 0.010695$	11 C -0.073377	-0.058528
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16161.158042 -0.000300 16H0.2038700.00085317H0.2187230.00253718H0.209975 -0.000943 19CI0.1225460.01953920CI0.0930030.01069921O -0.652057 0.11170022C0.118945 -0.00790 24N -0.773321 0.00143125C0.2377010.00814726C -0.607494 -0.001845 27N -0.091427 -0.144520 28H0.226024 -0.000478 29H0.226076 0.00355 30H0.235029 -0.000565 31O -4.29463 -0.114264 32H 0.429463 -0.114264 33Co 1.340873 1.438155 34C -0.016203 0.006030 35C 0.229215 -0.093833 37C -0.116203 0.006030 38C -0.125239 -0.01174 39C -0.073385 -0.00943 42H 0.158045 -0.000853 44C 0.032574 -0.00943 42H 0.158045 -0.000853 44C 0.032574 -0.00943 42H 0.158045 -0.000853 44C 0.012577 -0.074313 48C 0.232129 -0.0042411 <td< td=""><td>14 C 0.292569</td><td>-0.093809</td></td<>	14 C 0.292569	-0.093809
16 H 0.203870 0.000853 17 H 0.218723 0.002537 18 H 0.209975 -0.00943 19 CI 0.122546 0.019539 20 CI 0.093003 0.010699 21 O -0.652057 0.111700 22 C 0.118945 -0.003742 23 H 0.248345 -0.001431 25 C 0.237701 0.008147 26 C -0.607494 -0.001845 27 N -0.091427 -0.144520 28 H 0.235029 -0.000355 30 H 0.235029 -0.000565 31 O -0.429463 -0.114264 32 H 0.430873 -0.047717 35 C -1.01620 0.003258 36 C 0.225239 -0.01174 39 C -0.125239 -0.01174 39 C -0.125239 -0.01074 37 C -0.16203 0	15 H 0.158042	-0.000300
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18 H 0.20975 -0.00943 19 CI 0.122546 0.019539 20 CI 0.093003 0.010699 21 O -0.652057 0.111700 22 C 0.118945 -0.03742 23 H 0.248345 -0.00790 24 N -0.773321 0.001431 25 C 0.237701 0.008145 27 N -0.091427 -0.144520 28 H 0.232924 -0.000478 29 H 0.266076 0.000355 30 H 0.235029 -0.000555 31 O -429463 -0.114264 32 H 0.431038 0.004678 33 Co 1.340873 1.438155 34 C -0.023515 -0.093833 37 C -0.116203 0.006030 38 C -0.22515 -0.093833 37 C -0.118724 0.002537 41 H 0.20871 -0.00	17 H 0.218723	0.002537
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 0.235029 -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 -0.009433 42 H 0.158045 -0.003000 43 H 0.203871 0.000853 44 C 0.032528 -0.023261 45 C -0.147227 0.074313 48 C 0.560029 -0.042441 49 C -0.107867 0.056592 50 H 0.232170 0.008156 51 H 0.234709 -0.001357 53 C 0.237705 0.008156 54 H 0.231705 0.008156 55 N -0.091426 -0.144563 56 O -0.429458 -0.114289 57 H 0.431041 0.004679 58 H 0.23229 -0.000565 59 H 0.232292 -0.000565 59 H 0.232292 -0.000565 59 H 0.232928 -0.003555 50 C -0.429458 -0.114289 57 H 0.431041 0.004679 58 H 0.232129 0.000555 59 H 0.232928 -0.000565 59 H 0.232928 -0.000565 59 H 0.232928 -0.000565 59 H 0.232928 -0.000565 59 H 0.232928 -0.000575 50 C -0.429458 -0.114289 57 H 0.431041 0.004679 58 H 0.232928 -0.000565 59 H 0.232928 -0.000575 59 H 0.232928 -0.000798 50 C -0.128931 -0.00798 50 C -0.128931 -0.00798 50 C -0.128931 -0.00798 50 C -0.128931 -0.00798 50 C -0.129343 -0.00798 50 C -0.129343 -0.00798 50 C -0.129343 -0.00798 50 C -0.1293451 -0.003951	18 H 0.209975	-0.000943
$\begin{array}{c} 10 & 0.0 & 0.01069 \\ 21 & 0 & -0.652057 & 0.111700 \\ 22 & C & 0.118945 & -0.033742 \\ 23 & H & 0.248345 & -0.000790 \\ 24 & N & -0.773321 & 0.001431 \\ 25 & C & 0.237701 & 0.008147 \\ 26 & C & -0.607494 & -0.001845 \\ 27 & N & -0.091427 & -0.144520 \\ 28 & H & 0.232024 & -0.000478 \\ 29 & H & 0.232024 & -0.000555 \\ 31 & O & -0.429463 & -0.114264 \\ 32 & H & 0.431038 & 0.004678 \\ 33 & Co & 1.340873 & 1.438155 \\ 34 & C & -0.083073 & -0.047717 \\ 35 & C & -0.116142 & 0.033258 \\ 36 & C & 0.292515 & -0.093833 \\ 37 & C & -0.116203 & 0.006030 \\ 38 & C & -0.125239 & -0.010174 \\ 39 & C & -0.073385 & -0.058565 \\ 40 & H & 0.218724 & 0.002537 \\ 41 & H & 0.20974 & -0.000943 \\ 42 & H & 0.158045 & -0.003000 \\ 43 & H & 0.203871 & 0.000853 \\ 44 & C & 0.032528 & -0.023261 \\ 45 & C & -0.364445 & 0.080567 \\ 46 & C & 0.132871 & -0.059100 \\ 47 & C & -0.417227 & 0.74313 \\ 48 & C & 0.560029 & -0.042441 \\ 49 & C & -0.017867 & 0.055592 \\ 50 & H & 0.232129 & 0.000637 \\ 51 & H & 0.234219 & 0.000637 \\ 51 & H & 0.234219 & 0.000837 \\ 53 & C & 0.037105 & 0.008156 \\ 54 & C & -0.607494 & -0.01846 \\ 55 & N & -0.091426 & -0.144563 \\ 55 & N & -0.091426 & -0.00355 \\ 56 & H & 0.235032 & -0.000565 \\ 59 & H & 0.248343 & -0.000798 \\ 63 & O & -0.652082 & 0.111658 \\ 64 & C & 0.093306 & 0.010695 \\ 67 & H & 0.125577 & H \\ 0.125577 & H & 0.125577 \\ 0 & H &$	19 CL 0 122546	0.019539
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20 C1 0.093003	0.010699
2 C 0.118945 -0.033742 2 C 0.118945 -0.033742 2 H 0.248345 -0.000790 2 N -0.773321 0.001431 2 S C 0.237701 0.008147 2 G C -0.607494 -0.001845 2 N -0.091427 -0.144520 2 B H 0.235029 -0.000565 3 O H 0.235029 -0.000565 3 O -0.429463 -0.114264 3 2 H 0.431038 0.004678 3 3 Co 1.340873 1.438155 3 4 C -0.083073 -0.047717 3 5 C -0.110142 0.033258 3 6 C 0.292515 -0.093833 3 7 C -0.110142 0.032528 3 6 C 0.292515 -0.093833 3 7 C -0.116123 0.00630 3 8 C -0.125239 -0.010174 3 9 C -0.073385 -0.658565 4 0 H 0.218724 0.002537 4 1 H 0.20974 -0.000943 4 2 H 0.158045 -0.000300 4 3 H 0.203871 0.000853 4 4 C 0.032528 -0.023261 4 5 C -0.364445 0.080567 4 6 C 0.1322871 -0.059100 4 7 C -0.417227 0.074313 4 8 C 0.560029 -0.042441 4 9 C -0.107867 0.056592 5 0 H 0.232129 0.000637 5 1 H 0.25438 0.002102 5 2 N -0.773322 0.001357 5 3 C 0.237705 0.008156 5 4 C -0.607494 -0.001846 5 5 N -0.091426 -0.144563 5 6 O -0.429458 -0.114289 5 7 H 0.431041 0.004679 5 8 H 0.235032 -0.000555 6 1 C 0.118930 -0.033528 6 2 H 0.232208 -0.000477 6 0 H 0.26076 0.000355 6 1 C 0.118930 -0.033528 6 2 H 0.248343 -0.000798 6 3 O -0.652082 0.111658 6 4 C 0.0132571 0.008156 5 5 C H 0.23209 0.000477 5 1 H 0.248343 -0.000798 5 6 C 0.013292 0.000477 5 1 H 0.248343 -0.000798 5 5 0 H 0.23209 0.00355 5 5 1 H 0.23409 0.033528 5 0 H 0.23209 0.000655 5 9 H 0.23209 0.000798 6 0 O -0.652082 0.111658 6 4 C 0.012951	20 01 0.055005	0.111700
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 $0.20974 - 0.000943$ 42 H $0.158045 - 0.00300$ 43 H $0.203871 - 0.00853$ 44 C $0.032528 - 0.023261$ 45 C $-0.364445 - 0.080567$ 46 C $0.132271 - 0.073131$ 48 C $0.560029 - 0.042441$ 49 C $-0.107867 - 0.05592$ 50 H $0.232129 - 0.001377$ 51 H $0.254638 - 0.002102$ 52 N $-0.773322 - 0.001357$ 53 C $0.237705 - 0.008156$ 54 C $-0.367444 - 0.001846$ 55 N $-0.091426 - 0.144563$ 56 O $-0.429458 - 0.114289$ 57 H $0.235032 - 0.000477$ 58 H $0.235032 - 0.000477$ 60 H $0.236076 - 0.003555$ 59 H $0.232928 - 0.000477$ 60 H $0.236076 - 0.003555$ 50 C $-0.429458 - 0.114289$ 57 H $0.235032 - 0.000477$ 58 H $0.235032 - 0.000477$ 59 H $0.232928 - 0.000477$ 50 H $0.236076 - 0.003555$ 50 H $0.232702 - 0.003555$ 51 C $-0.0607494 - 0.001846$ 55 N $-0.091426 - 0.144563$ 56 O $-0.429458 - 0.1103807$ 57 H $0.235032 - 0.000355$ 50 H $0.236702 - 0.000477$ 51 H $0.248343 - 0.000798$ 53 O $-0.652082 - 0.111658$ 54 C $-0.073006 - 0.010695$ 55 P H $0.237702 - 0.01357$ 55 P H $0.237702 - 0.01357$ 55 P H $0.237702 - 0.003555$ 56 C C $0.018930 - 0.033628$ 57 C $0.019306 - 0.010695$ 59 C D $0.028773 - 0.010575$ 50 C $0.028773 - 0.010575$ 51 C $0.019306 - 0.010695$ 52 C $0.027770 - 0.010565$ 53 C $0.028772 - 0.010575$ 54 C $0.0293006 - 0.010695$ 55 C C $0.0293006 - 0.010695$ 55 C C $0.018930 - 0.033628$ 56 C C $0.0293006 - 0.010695$ 57 C C $0.027708 - 0.001695$ 56 C C $0.0125273 - 0.010571$ 51 C $0.0125273 - 0.010571$ 51 C $0.0125273 - 0.010571$ 51 C $0.0125273 - 0.010571$ 51 C 0.0125	22 C 0 118945	-0.033742
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22 C 0.110745 23 H 0.248345	-0.000790
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25 11 0.240545 24 N _0 773321	0 001431
26 C $-0.607494 -0.001845$ 27 N $-0.091427 -0.144520$ 28 H $0.235029 -0.000565$ 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 $0.158045 -0.00300$ 43 H $0.203871 -0.003853$ 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 $0.50029 -0.042441$ 49 C $-0.107867 0.056592$ 50 H $0.232129 0.000637$ 51 H $0.232129 0.000637$ 52 N $-0.071332 -0.001357$ 53 C $0.237705 0.008156$ 54 C $-0.607494 -0.01846$ 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 $0.26076 0.00355$ 61 C $0.118930 -0.033628$ 62 H $0.248343 -0.00798$ 63 O $-0.652082 0.111658$ 64 C I $0.093006 0.010695$	27 11 -0.77321 25 C 0 237701	0 008147
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25 C 0.257701 26 C -0.607494	-0.001845
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20 C -0.007494 27 N -0.091427	-0.144520
20 H 0.26076 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 -0.25239 -0.010174 39 C -0.073385 -0.058565 40 H 0.218724 0.002537 41 H 0.20974 -0.000943 42 H 0.158045 -0.00300 43 H 0.203871 0.000853 44 C 0.032528 -0.023261 45 C -0.347445 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 -0.01846 55 N -0.091426 -0.144563 56 O -0.429488 -0.114289 57 H 0.4330441 0.004679 58 H 0.235032 -0.000477 60 H 0.236076 0.00355 61 C 0.118930 -0.033628 62 H 0.248343 -0.00798 63 O -0.652082 0.111658 64 C1 0.093006 0.010695	28 H 0 232924	-0.000478
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20 H 0.252524 29 H 0.266076	0.000355
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	30 H 0.235029	-0.000565
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	31 0 -0.429463	-0.114264
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	31 U -0.429403 32 H 0.431038	0.004678
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	32 H 0.451050 33 Co 1 340873	1 438155
$\begin{array}{c} 35 \ C & -0.110142 & 0.033258 \\ 36 \ C & 0.292515 & -0.093833 \\ 37 \ C & -0.116203 & 0.006030 \\ 38 \ C & -0.25239 & -0.010174 \\ 39 \ C & -0.073385 & -0.058565 \\ 40 \ H & 0.218724 & 0.002537 \\ 41 \ H & 0.209974 & -0.000943 \\ 42 \ H & 0.218712 & 0.000300 \\ 43 \ H & 0.203871 & 0.000853 \\ 44 \ C & 0.032528 & -0.03261 \\ 45 \ C & -0.364445 & 0.080567 \\ 46 \ C & 0.132871 & -0.059100 \\ 47 \ C & -0.417227 & 0.074313 \\ 48 \ C & 0.560029 & -0.042441 \\ 49 \ C & -0.107867 & 0.056592 \\ 50 \ H & 0.232129 & 0.000637 \\ 51 \ H & 0.254638 & 0.002102 \\ 52 \ N & -0.773322 & 0.001357 \\ 53 \ C & 0.237705 & 0.008156 \\ 54 \ C & -0.607494 & -0.01846 \\ 55 \ N & -0.091426 & -0.144563 \\ 56 \ O & -0.429458 & -0.114289 \\ 57 \ H & 0.431041 & 0.004679 \\ 58 \ H & 0.235032 & -0.000565 \\ 59 \ H & 0.232928 & -0.000477 \\ 60 \ H & 0.260076 & 0.00355 \\ 61 \ C & 0.118930 & -0.033628 \\ 62 \ H & 0.248343 & -0.00798 \\ 63 \ O & -0.652082 & 0.111658 \\ 64 \ C1 & 0.093006 & 0.010695 \\ \end{array}$	34 C -0 083073	-0.047717
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	34 C -0.003073 35 C -0.110142	0.033258
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	36 C 0 292515	-0.093833
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	37 C -0 116203	0.006030
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	37 C -0.110203 38 C -0.125239	-0 010174
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	30 C -0.073385	-0.058565
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	40 H 0 218724	0.002537
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	40 H 0.210724 41 H 0.209974	-0 000943
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	42 H 0.158045	-0.000300
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	43 H 0 203871	0.000853
$\begin{array}{c} 45 \ C & -0.36445 & 0.080567 \\ 46 \ C & 0.132871 & -0.059100 \\ 47 \ C & -0.417227 & 0.074313 \\ 48 \ C & 0.560029 & -0.042441 \\ 49 \ C & -0.107867 & 0.056592 \\ 50 \ H & 0.232129 & 0.000637 \\ 51 \ H & 0.254638 & 0.002102 \\ 52 \ N & -0.773322 & 0.001357 \\ 53 \ C & 0.237705 & 0.008156 \\ 54 \ C & -0.607494 & -0.001846 \\ 55 \ N & -0.091426 & -0.144563 \\ 56 \ O & -0.429458 & -0.114289 \\ 57 \ H & 0.431041 & 0.004679 \\ 58 \ H & 0.235032 & -0.000565 \\ 59 \ H & 0.232928 & -0.000477 \\ 60 \ H & 0.26076 & 0.000355 \\ 61 \ C & 0.118930 & -0.033628 \\ 62 \ H & 0.248343 & -0.00798 \\ 63 \ O & -0.652082 & 0.111658 \\ 64 \ C1 & 0.093006 & 0.010695 \\ 65 \ C1 & 0.12527 & 0.019521 \\ \end{array}$	44 C 0.032528	-0.023261
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	45 C -0.364445	0.080567
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	46 C 0.132871	-0.059100
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	47 C -0.417227	0.074313
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	48 C 0.560029	-0.042441
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	49 C -0.107867	0.056592
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	50 H 0.232129	0.000637
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	51 H 0 254638	0.002102
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	52 N -0.773322	0.001357
$54 \ C -0.00749 - 0.001846$ $55 \ N -0.091426 - 0.144563$ $56 \ O -0.429458 - 0.114289$ $57 \ H \ 0.431041 \ 0.004679$ $58 \ H \ 0.235032 - 0.000565$ $59 \ H \ 0.235032 - 0.000477$ $60 \ H \ 0.26076 \ 0.000355$ $61 \ C \ 0.118930 - 0.033628$ $62 \ H \ 0.248343 - 0.000798$ $63 \ O -0.652082 \ 0.111658$ $64 \ C1 \ 0.093066 \ 0.010695$ $65 \ C1 \ 0.125237 \ 0.010521$	53 C 0.237705	0.008156
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	54 C -0.607494	-0.001846
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	55 N -0.091426	-0.144563
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58 H 0.235032 -0.000565 59 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 0.010521	57 H 0.431041	0.004679
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	58 H 0.235032	-0.000565
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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 0.125237 0.019521	60 H 0.266076	0.000355
62 H 0.248343 -0.000798 63 O -0.652082 0.111658 64 Cl 0.093006 0.010695 65 Cl 0.12257 0.019521	61 C 0.118930	-0.033628
63 O -0.652082 0.111658 64 Cl 0.093006 0.010695 65 Cl 0.12257 0.019521	62 H 0 248343	-0.000798
64 Cl 0.093006 0.010695 65 Cl 0.12537 0.010691	63 O -0.652082	0.111658
65 CL 0122537 0.010521	64 CL 0.093006	0.010695
03 (1 0.14433/ 0.017341	65 Cl 0.122537	0.019521

Sum of Mulliken charges = 2.00000 spin density=1.00000

Vibrational analysis

The molecular vibrations of the (3,5dichlorosalicyliden-*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 (3,5dichlorosalicyliden-*p*-iminoacetophenone oxime).



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

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



Fig. 5: Experimental IR spectrum of the complexes.

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

 $\begin{aligned} & 2LH+Co(CH_3COO)_2\bullet 4H_2O \rightarrow Co(L)_2+2CH_3COOH+4H_2O\\ & 2LH+Ni(CH_3COO)_2\bullet 4H_2O \rightarrow Ni(L)_2+2CH_3COOH+4H_2O\\ & 2LH+Cu(CH_3COO)_2\bullet H_2O \rightarrow Cu(L)_2+2CH_3COOH+H_2O\\ & 2LH+Zn(CH_3COO)_2\bullet 2H_2O \rightarrow Zn(L)_2+2CH_3COOH+2H_2O \end{aligned}$

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: ¹H-NMR spectrum of the Zn (II) complex.

Characteristic ¹H-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 (CH₃). The phenolic OH signal, which had acidic proton at 13.09 ppm, disappeared with D₂O in the solution. The peak of the O-H group observed in the ligand in the ¹H-NMR spectrum of the Zn(II) complex is not observed. The peak of the O-H group observed in the ligand in the ¹H-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 ¹³C-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 ¹³C-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: ¹³C-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 nonbonding 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 ($\varepsilon = 151-196 \text{ L mol}^{-1} \text{ cm}^{-1}$), 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 ($\epsilon = 1.52-3.93 \text{ X} 10^3 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$), which can be assigned to charge transfer transition of tetrahedral geometry [30-32].

Compounds	Formula	F.W(g/mol)	Color	Yield(%)	µeff(B.M.)	Elemental analysisCalculated (found) (%)		
						С	н	Ν
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	CoC30H22Cl4N4O4	703.27	light red	65	4.04	51.24 (50.88)	3.15 (2.79)	7.97 (8.37)
Ni(L)₂	NiC30H22Cl4N4O4	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 ₄ N ₄ O ₄	707.88	light brown	59	1.80	50.90 (51.12)	3.13 (2.73)	7.91 (8.30)
Zn(L) ₂								
	ZnC30H22Cl4N4O4	709.74	light yellow	67	dia	50.77 (51.15)	3.12 (2.72)	7.89 (8.27)

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

Thermal studies

Thermogravimetric (TG) curves were recorded as a result of combustion of the synthesized complex compounds in the N2 atmosphere at 20-800 °C with an increase of 10 °C 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, ¹H and ¹³C 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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