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Synthesis, Spectral Characterization, Thermal and Theoretical Studies of Two Co(II) and Ni(II) Coordination Complex with N, O Donor of 2-Chloro-6-[(3-hydroxy-4-methoxybenzylidene) amino]-4-Nitrophenol

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ABSTRACT

We report here two mononuclear Co(II) and Ni(II) complexes of general formula $[M(L)_2(H_2O)_2]$*.* xH_2O*, {M:*Co^{II} *and* Ni^{II}*; x:2} derived from 2-chloro-6-[(3-hydroxy-4-methoxybenzylidene) amino]-4-nitrophenol ligand. Synthesized compounds were characterized by elemental analysis, FT-IR, UV-Visible, molar conductance, thermal, PXRD and SEM. Distorted octahedral geometry was suggested for both complexes around the metal center with ligand. The Powder X-ray diffraction pattern and SEM analysis shows the crystalline nature of complexes. Thermal studies of the synthesized complexes show their general decomposition pattern and thermal stability. The kinetic and thermodynamic parameters viz. activation energy (*E^**), entropy of activation (*ΔS^**), enthalpy of activation (*ΔH^**) and free energy of activation (*ΔG^**) of degradation process were also evaluated using Coats-Redfern (C-R) and Horowitz–Metzger (H-M) methods for both complexes assuming first order degradation. In addition theoretical calculations by means of DFT at B3LYP level were incorporated to support the experimental findings.*

Graphical Abstract

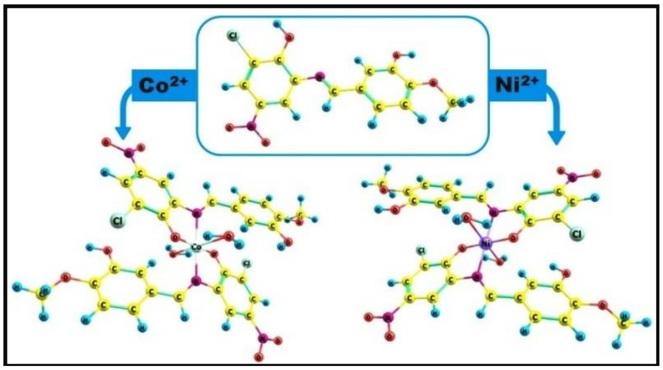

Figure 7. DFT optimized Structure of ligand (HL) using B3LYP/6-31G basis set and its Co (II)- and Ni(II)-complex using B3LYP/LANL2DZ basis set.

Keywords: Schiff base-metal complexes, Thermal studies, Electrochemical studies, XRD, DFT.

INTRODUCTION

The study of coordination compounds has facilitated the inorganic chemists to make progressive efforts in refining the concept of chemical bonding and to explain persuade of bonding, on the various properties of the compounds. A designed Schiff base in metal coordination sphere can fabricate specific functionalities and exciting features which make an interesting subject of theoretical studies and realistic applications. The complexes with such types of Schiff bases have received immense interest due to their structural diversity, versatile binding modes and promising biological and material applications [**1-3**]. Many Schiff-base complexes of cobalt and nickel had been reported which were studied widely for their interesting biological applications [**4-6**]. These compounds were effectively developed as sensor [**7**], luminescence materials [**8**] and efficient catalysts in many organic synthesis such as in polymerization, olefin oxidation etc. [**9**].

In recent year's theoretical studies of coordination compounds by means of DFT are gained much more interest and grown as an important tool to correlate and explain their structural features and properties. DFT calculations set an option for the prediction of fairly accurate three dimensional structures of the compounds where the quality of single crystals is not yielded [**10-11**].

In present paper, the synthesis and spectral characterization of Schiff-base ligand derived from 3-hydroxy-4-methoxybenzaldehydeand 2-amino-6-chloro-4-nitrophenoland its mononuclear Co(II) and Ni(II) complexes were reported. In addition, DFT calculations of synthesized compounds were also carried out to support the experimental findings.

MATERIALS AND METHODS

Reagents and instruments: All the reagents were obtained (3-hydroxy-4-methoxybenzaldehyde, Mol. Wt. 152.15 g mol^{-1}, $CoCl_2.6H_2O$, Mol. Wt. 237.93 g mol^{-1}, $NiCl_2.6H_2O$, Mol. Wt. 237.69 gmol^{-1} from Aldrich, India and 2-amino-6-chloro-4-nitrophenol, Mol. Wt. 188.57g mol^{-1} from Metropolitan Eximchem. Ltd., India) with analytical grade and used as such. Elemental analysis (C, H and N) had been done in Thermo Scientific (FLASH 2000) CHN Elemental Analyzer at Sophisticated Analytical Instrument Facility (SAIF), Panjab University, Chandigarh, India. Molar conductance of complexes was recorded in DMF (10^{-3} M) at room temperature using Systronic model-304 digital conductivity meter. The FTIR spectra were recorded as KBr discs in the range of 4000–400 cm^{-1} on a Shimadzu FT IR-8400S instrument. The UV-Visible spectra were recorded in DMF using Systronics double beam UV-Visible Spectrophotometer over the range of 900-200 nm at room temperature. Thermal data were collected on a NETZSCH STA instrument under nitrogen atmosphere at the heating rate of 10K min^{-1} from room temperature to 1073 K. X-ray powder diffraction patterns of the samples were recorded at room temperature on a Brucker D-8 Advances X-ray diffractometer using Cu Kα radiation (1.5418 A^{o}) operating at 35 kV (2θ= 5-70 °).SEM studies were carried out on scanning electron microscope FEI NOVA Nano SEM 450 with the accelerating voltage of 15 kV in liquid nitrogen atmosphere.

Synthesis of 2-chloro-6-[(3-hydroxy-4-methoxybenzylidene)amino]-4-nitrophenol: 3-hydroxy-4-methoxybenzaldehyde, (20 mmol) was taken in 40 mL of ethanol, to which ethanolic solution of 2-amino-6-chloro-4-nitrophenol, (20 mmol; 40 mL) was added drop wise with stirring. Instantly, a red colored solution was obtained. To facilitate completion of the condensation reaction; stirring was unrelenting for 30 min at 70^{o}C. The progress of reaction was examined with the help of TLC. The red colored product thus obtained was filtered off, washed with methanol and ether, recrystallized in ethanol and dried *in vacuo* over fused $CaCl_2$. Mol. Formula: $C_{14}H_{11}ClN_2O_5$; Mol. Wt.: 322.7; Yield: 78%; Color: red, Anal. Calc.(%): C-52.11, H-3.44, N-8.68, Cl-10.99, O-24.79; Found(%): C-52.32, H-3.48, N-8.52; FTIR (KBr) cm^{-1}: 1545-1650 ($\upsilon_{C=C\ aromatic}$), 1625 ($\upsilon_{C=N}$), 1255-1340 (υ_{C-O}), 1115-1310 (υ_{C-N}), 3525-3720 (υ_{O-H}), 3025-3145 (υ_{C-H}); UV-Vis(DMF) λ (nm): 465.4, 308.4;

Synthesis of the metal complexes [ML_2] {M =Co(II) and Ni(II)}: The metal(II) chlorides (5 mmol), were taken in minimum volume of ethanol (~20 ml)and added drop wise to the ethanolic solution of Schiff base (10 mmol) in presence of aq. KOH solution, the mixture was stirred and refluxed for 1 h. During this period, precipitation were observed for both complexes, further those colored precipitates were filtered under the hot conditions, washed with ethanol and diethyl ether and dried *in vacuum* over fused $CaCl_2$.

[$Co(L)_2(H_2O)_2$].$2H_2O$: Mol. Formula: $C_{28}H_{24}Cl_2N_4CoO_{12}$; Mol. Wt.: 738.3; Yield 68%; Color: brown; stable; readily soluble in DMF and DMSO, insoluble in non-polar solvents. Anal. Calc.: C-45.51, H-3.28, N-7.58, Cl-9.61, O-26.00, Co-7.98; Found: C-45.78, H-3.34, N-7.44; Molar conductance (DMF) λ_m: 44.8cm$^2\Omega^{-1}$mol^{-1}; FTIR (KBr) cm^{-1}: 1470-1545 ($\upsilon_{C=C\ aromatic}$), 1588 ($\upsilon_{C=N}$), 1215-1325 (υ_{C-O}), 1115-1220 (υ_{C-N}), 3660-3720 (υ_{O-H}), 2985-3125 (υ_{C-H}), 505(υ_{M-O}),455(υ_{M-N}); UV-Vis(DMF) λ (nm): 435.2, 415.6, 288.4.

[$Ni(L)_2(H_2O)_2$].$2H_2O$: Mol. Formula: $C_{28}H_{24}Cl_2N_4NiO_{12}$; Mol. Wt.: 738.1; Yield 66%; Color: brownish green; stable; readily soluble in DMF and DMSO, insoluble in non-polar solvents. Anal. Calc.: C-45.52, H-3.28, N-7.58, Cl-9.62, O-26.01, Ni-7.95; Found: C-45.86, H-3.42, N-7.46; Molar conductance (DMF) λ_m:40.4cm$^2\Omega^{-1}$mol^{-1}; FTIR (KBr) cm^{-1}: 1410-1560 ($\upsilon_{C=C\ aromatic}$), 1602 ($\upsilon_{C=N}$), 1170-1310 (υ_{C-O}), 1160-1230 (υ_{C-N}), 3620-3710 (υ_{O-H}), 2970-3210 (υ_{C-H}), 560(υ_{M-O}),465(υ_{M-N}); UV-Vis(DMF) λ (nm): 472.2, 416.0, 296.0.

Theoretical Calculations: The entire theoretical Calculations of ligand and its complexes were performed at DFT level employing B3LYP using the 6-31G and LANL2DZ basis set with the help of Gaussian 03W and Gauss view 3.0 software [12-14]. Furthermore, visualization of optimized structures was performed by means of Chemcraft 1.7 program package [15]. The molecular of geometries of all the compounds were optimized in gas phase using B3LYP/6-31G and B3LYP/LANL2DZ basis set and no symmetry restrains were applied.

RESULTS AND DISCUSSION

The physical and analytical data of synthesized compounds suggest that the ligand associates with metal ions in 1:2 (M:L) molar ratio and form the metal complexes of general composition [$M(L)_2(H_2O)_2$].$2H_2O$ (M = Co^{II} and Ni^{II}). All complexes were colored, stable at room temperature and insoluble in most common organic solvents except DMF and DMSO. The molar conductance measurements of the complexes were recorded in DMF ($1x10^{-3}$ M). The results indicate their non-electrolytic nature. The synthetic scheme and suggested structure of ligand and complexes studied in present work were shown in figure 1.

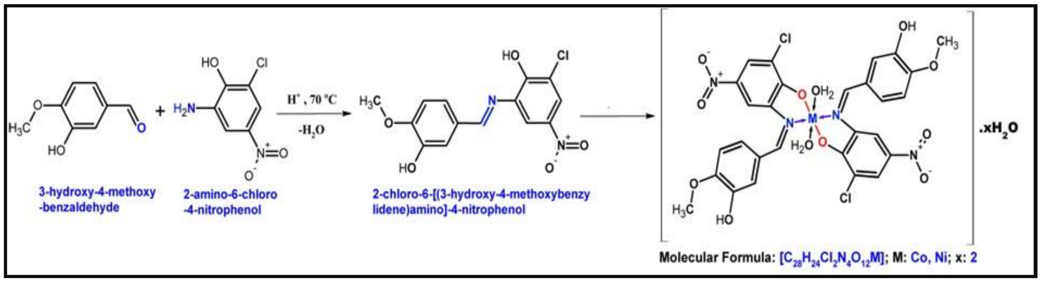

Figure 1. Synthetic scheme and possible molecular structure of ligand and it's complexes.

FT-IR and electronic spectral studies: The ligand show some characteristic vibrational bands of the (—HC=N—), (C—O), (O—H) and (—NO_2) groups at 1625, 1255-1340, 3525-3720 and 1115-1310 cm^{-1} respectively. To find out the coordination modes of ligand, FT-IR spectra of the complexes were compared with parental Schiff base ligand. The combined FT-IR spectra in the range of 4000–400

cm^{-1} were shown in figure 2. The characteristic azomethine stretching band shifted to lower wave numbers in complexes (1588 cm^{-1} for Co and 1602 cm^{-1} for Ni complex) due to the participation of azomethine N atom in coordination. Two new weak bands were appeared in complexes in the range of 505-560 cm^{-1} and 455-465 cm^{-1}which represent the M–O and M–N stretching vibrations respectively. In complexes two new additional bands were observed at 730-742 cm^{-1} and 668-676 cm^{-1} corresponding to $\delta_r(H_2O)$ rocking and $\delta_w(H_2O)$ wagging vibrations respectively of coordinated water molecules. Further a broad band at 3400-3700 cm^{-1} due to (H_2O) stretching vibrations in both complexes was also appeared. These bands were not observed in the ligand spectrum [16-17].

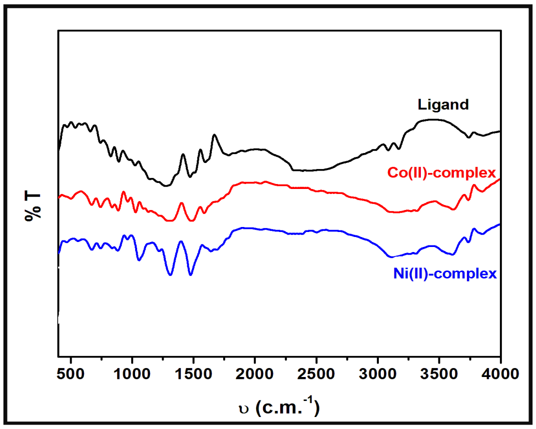

Figure 2. FT-IR spectra of Schiff base ligand, Co(II) complex and Ni (II) complex in the range of 400-4000 cm^{-1}.

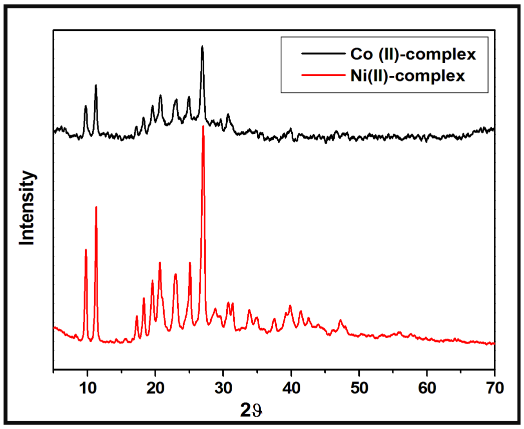

Figure 3. Powder x-ray diffraction patterns of Co(II) and Ni(II) complexes showing in the range of 5-70° (2θ).

The electronic absorption spectra of ligand and its Co(II) and Ni(II) complexes were recorded in DMF solvent. The ligand absorbs at very high wavelength of 465.4 nm and 308.4 nm corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively. The $n \rightarrow \pi^*$ transition occur at longer wavelength may be due to the presence of electron withdrawing substituent such as ─Cl, which cause a red-shift of peak position. In complexes the position of those bands were altered and a new band appeared at 415.6 nm and 416 nm respectively correspond to LMCT transitions. [18-19].

Powder X-ray diffraction and SEM Studies: Now a day's Powder XRD has gained quite attention as a technique to explain the structural feature of inorganic compounds in the absence of single crystal XRD data. This method is quite useful to bind up the structure, size and strain of the synthesized compounds [20]. In powder X-ray diffraction analysis, Co(II) and Ni(II) complexes exhibit sharp peaks showing their crystalline nature as shown in figure 3. The most intense peak (I_{max}) were found at 26.92° (2θ) with *d*-spacing value of 3.3093for Co(II) complex and 27.06° (2θ) with *d*-spacing value of 3.2925 for Ni(II) complex.

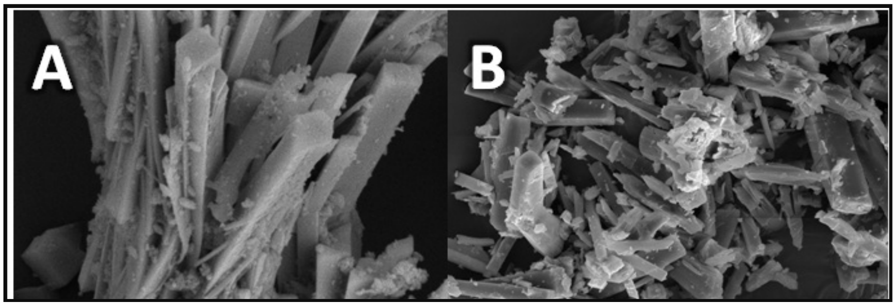

Figure 4. Scanning electron micrograph for gold coated (A) Co(II)-complex and (B) Ni(II)-complex.

The SEM analysis had been performed for the surface morphological studies and the micrographs obtained were represented in figure 4. The SEM images also support the crystalline nature of Co(II) and Ni(II)-complex which appeared as well defined small rod shape. All the crystals were found to grow up from just a single molecule to several molecules with different particle sizes [21].

Thermal studies: In a thermogram of metal complex, lattice water is eliminated first in the range of ~320-390 K followed by coordinated water molecules in the range of ~390-525 K. To understand the thermal behavior of those complexes, the TG curves were shown in figure 5 and 6.

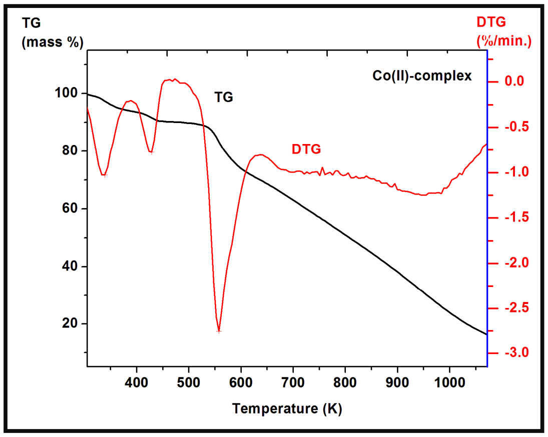

Figure 5. Thermogram plot of Co(II)-complex showing TG as black line and DTG as red line respectively up to 1172 K.

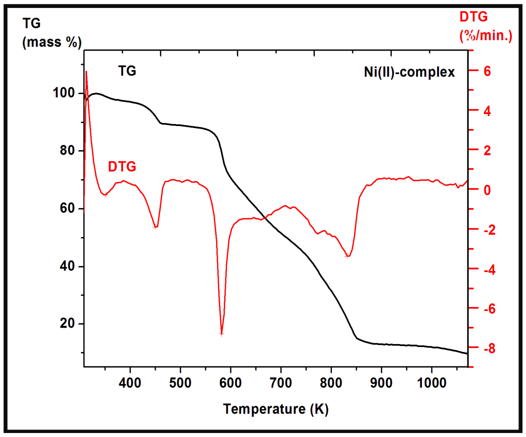

Figure 6. Thermogram plot of Ni(II)-complex showing TG as black line and DTG as red line respectively up to 1172 K.

In TGA curve of the $[Co(L)_2(H_2O)_2].2H_2O$ complex; 4.95% (calc. 4.65%) weight loss were monitored in the first step (312-375K) corresponding to two molecules of lattice water and 4.31% (calc. 4.65%) weight loss corresponding to two molecules of coordinated water had been observed in the second step (390-440K). In third step (490-615 K), the non-chelated part of the organic moiety assigned to 33.12% (calc. 33.45%) of total weight in the complexes was degraded. Remaining chelated part of the organic moiety was degraded continuously up to the final temperature 1172 K and the final pyrolysis product, projected as cobalt (II) oxide CoO with some other by-products of 16.13% (calc. 9.68%) of total mass had been observed. The quite similar results had been observed in the TG curve of the $[Ni(L)_2(H_2O)_2].2H_2O$ complex where degradation pattern were explained in three steps; in first step 9.52% (calc. 9.30%) of total weight corresponding to two molecules of lattice and coordinated water each which were lost in the range of 330-480 K. In second step (540-610 K); non-chelated part of the organic moiety was eliminated which were found to be 34.29% (calc. 33.46%). In the last step (705-890 K); 46.79% (calc. 47.55%) weight loss were marked corresponding to remaining chelated organic part of the ligand and gives the ultimate pyrolysis product as nickel(II) oxide, NiO with some additional unreacted residue of mass 9.68% (calc. 9.43%) [22-23].

Kinetic study: The kinetic and thermodynamic parameters *viz.* activation energy (E^*), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and free energy of activation (ΔG^*) of thermal degradation process had been evaluated using Coats-Redfern (C-R) [24] and Horowitz–Metzger (H-M) [25] methods. The degradation of Co(II) and Ni(II) complexes were assumed to be first order (n=1) in all the degradation steps. The calculated kinetic parameters were summarized in table 1.

Quite similar pattern were observed in both methods C-R and H-M during the calculation of kinetic parameters for all decomposition steps of $[Co(L)_2(H_2O)_2].2H_2O$ and $[Ni(L)_2(H_2O)_2].2H_2O$ complex. The activation energy of the compound directly related to its thermal stability e.g. higher the E^*higher the stability of complexes. The activation energy E^*were found to be in the range of 0.043-0.110 kJ mol^{-1} calculated by C-R method for$[Co(L)_2(H_2O)_2].2H_2O$. Similarly, in $[Ni(L)_2(H_2O)_2].2H_2O$, activation energy E^*had been found to be in the range of 0.087-0.217 kJ mol^{-1} at the same method.

The E^*were found to be highest for II-step in cobalt complex and in the III-step for nickel complex which means both dehydrated complexes are more stable and facing less steric strain in this stage. The corresponding values of the entropy of activation ΔS^*were lie in the range of -0.086 to -0.222 kJ mol^{-1} for Co(II) complex and -0.095 to -0.190 kJ mol^{-1} for Ni(II) complex. The negative values of ΔS^* indicate that the activated complexes were more ordered structure than the reactants or intermediates and degrade at slower rate than normal [26-27].

Table 1. Kinetic and thermodynamic parameters E*, ΔS*, ΔH* and ΔG* of $[Co(L)_2(H_2O)_2].2H_2O$ and $[Ni(L)_2(H_2O)_2].2H_2O$ complexes calculated by C-R and H-M method.

Method	Decomposition Step (DTG peak in K)	r^2	Non-isothermal kinetic parameter			
			E (kJ mol^{-1})	ΔS (kJ $mol^{-1}K^{-1}$)	ΔH (kJ mol^{-1})	ΔG (x 10^2) (kJ mol^{-1})
			Co-Complex			
C-R	I (340.85)	0.993	0.0431	-0.2220	-2.7906	0.7289
	II (430.31)	0.994	0.1101	-0.0859	-3.4674	0.3349
	III (557.82)	0.992	0.0759	-0.2224	-4.5618	1.1953
H-M	I (340.85)	0.996	0.0415	-0.2220	-2.7922	0.7289
	II (430.31)	0.997	0.1324	-0.0859	-3.4452	0.2583
	III (557.82)	0.989	0.0446	-0.2203	-3.5329	0.7156
			Ni-Complex			
C-R	I (347.14)	0.999	0.0873	-0.0951	-2.7987	0.3024
	II (454.47)	0.992	0.0995	-0.1220	-3.6789	0.5179
	III (581.77)	0.990	0.2178	-0.0210	-4.6189	0.1683
	IV (836.38	0.994	0.1353	-0.1896	-6.8182	1.5177
H-M	I (347.14)	0.998	0.0861	-0.0951	-2.7999	0.2964
	II (454.47)	0.994	0.1184	-0.1220	-3.6599	0.3794
	III (581.77)	0.992	0.2532	-0.0210	-4.5835	0.1174
	IV (836.38	0.990	0.1628	-0.0951	-2.7987	0.3024

r^2: regression coefficient

Theoretical Calculations: The gas phase geometry for synthesized compounds in ground state was fully optimized with respect to the energy using the 6-31G and LANL2DZ basis set at B3LYP level. The DFT calculation supports the structural assignment from its spectroscopic data. The molecular structures of the compounds were shown in figure 7. All the bond lengths and bond angles in phenyl rings were found in the common range. The geometry optimization was validated by frequency calculations, which gave real values for all the obtained frequencies and no imaginary frequencies were found; which means that the structure has minimum potential energy. The orientation of the two benzene and phenolic rings in the ligand was defined by the torsion angles of C3—N9—C16—C18 [-5.862°] calculated at B3LYP/6-31G level.

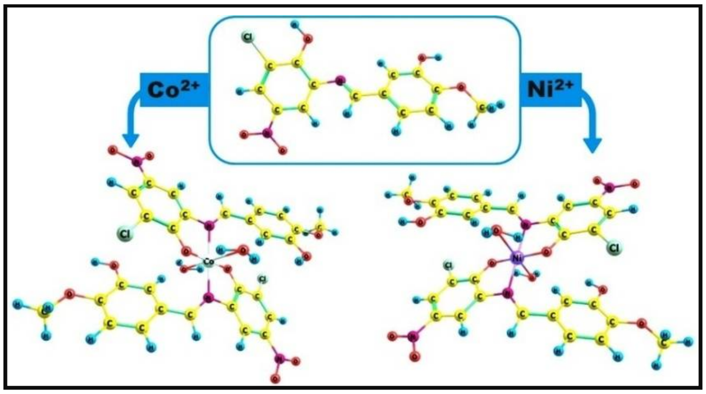

Figure 7. DFT optimized Structure of ligand (HL) using B3LYP/6-31G basis set and its Co (II)- and Ni(II)-complex using B3LYP/LANL2DZ basis set.

The azomethine group was coplanar with the benzene ring, as shown by the C19—C18—C16—N9 torsion angle of -8.714° and C20—C18—C16—N9 torsion angle of-173.253°. The calculated values of bond length of characteristic C16—N9 (azomethine) and C2—O10 (phenolic) had been found to be 1.286 $^{\circ}$A and 1.374 $^{\circ}$A respectively. The bond angles between C3—N9—C16; N9−C16—C18 and C3—C2—O10 calculated at B3LYP level were found to be 129.84°, 132.04° and 116.90° respectively.

In complexes; two ligand molecules were coordinated with metal ion through azomethine nitrogen and phenolic oxygen in a bidentate fashion, two water molecules also coordinated with central metal ions and acquired octahedral geometry around the metal center as revealed from the calculated bond lengths and bond angles. Quite similar results had been observed for Ni complexes. The Mulliken atomic charges for the ligand calculated at the B3LYP/6-31G level in gas-phase shows that the phenolic oxygen atom O is more negative (-0.593 and -0.617) as compared to azomethine nitrogen atom N (-0.378). same results has also been noticed in metal complex case; however the charges on phenolic oxygen atom O and azomethine nitrogen atom N get reduced due to charge distribution with central metal ions.

The experimental FT-IR data of ligand and its complexes had been compared with the calculated vibration frequencies using B3LYP/6-31G and B3LYP/LANL2DZ basis sets at DFT level. The theoretical group frequencies show little deviations from experimental values and appear at comparatively higher wave numbers which may be due to the negligence of an harmonicity in B3LYP method. However the theoretical-experimental agreement was found to be satisfactory [28].

APPLICATION

Two new mononuclear metal complexes are synthesized from 2-chloro-6-[(3-hydroxy-4-methox benzyli dene)amino]-4-nitrophenol. Characterized data reveals their structural geometry, their crystalline nature and highly thermal stability. The theoretical calculations also support the geometry of the complexes. Further these complexes may find wide applications in the field of material science and may act as an effective agents in biological activities like antimicrobial, antioxidant, DNA binding and DNA cleavage studies.

CONCLUSIONS

Interaction of bi dentate Schiff base ligand with cobalt and nickel ions results in two new mononuclear complexes. The spectral analysis of the resulted Schiff base-metal complexes revealed the structural arrangements. Both complex exhibits six coordinated distorted octahedral molecular geometry around metal center with two molecules of ligand and two molecules of water. They exhibit well defined sharp peaks in PXRD spectra showing their crystalline nature. Thermal studies showed a general degradation pattern as well as a high degree of thermal stability of the complexes. The kinetic and thermodynamic parameters *viz.* activation energy (E^*), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and free energy of activation (ΔG^*) of thermal degradation process had been evaluated using Coats-Redfern (C-R) and Horowitz–Metzger (H-M) methods assuming first order degradation. In addition theoretical calculations by means of DFT at b3lyp level had been incorporated to support the experimental findings for ligand and complexes.

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REFERENCES

[1]. A. Kochem, G. Gellon, O. Jarjayes, C. Philouze, A. D. M. Hardemare, M. V. Gastel, F. Thomas, *Dalton Trans.*, **2015**, DOI: 10.1039/c5dt00944h.

[2]. E. Loukopoulos, B. Berkoff, K. Griffiths, V. Keeble, V. Dokorou, A. Tsipis, A. Escuer, G. E. Kostakis*, Cryst. Eng. Comm*, **2015**, DOI: 10.1039/C5CE01294E.

[3]. A. Hens and K. K.Rajak, *RSC Adv.*, **2015**, 5, 4219-4232, DOI: 10.1039/c4ra13606c

[4]. W. Chen, Y. Li, Y. Cui, X. Zhang, H.-L. Zhu, Q. Zeng, *Euro J. Med. Chem.,* **2010**, 45, 4473-4478.

[5]. P. F. Salas, C. Herrmann, C. Orvig, *Chem. Rev.*, **2013**, 113, 3450-3492, dx.doi.org/ 10.1021/cr3001252

[6]. M. B. Ferrari, F. Bisceglie, C. Casoli, S. Durot, I. M. Badarau, G. Pelosi, E. Pilotti, S. Pinelli, P.Tarasconi, *J. Med. Chem.* **2005**, 48, 1671-1675, doi: 10.1021/jm049529n

[7]. A. A. A. Aziz, A. H. Kamel, *Talanta*, **2010**, 80, 1356-1363, doi:10.1016/j.talanta. 2009.09.036

[8]. M. Barwiolek, E. Szlyk, T. M. Muziołand T. Lis, *Dalton Trans.*, **2011**, 40, 11012-11022, DOI: 10.1039/c1dt10882d

[9]. K. C. Gupta, A. K. Sutar, *Coord. Chem. Reviews,* **2008**, 252**,** 1420–1450.

[10]. S. Cañellas, A. Bauza, A. Lancho, A. Garcia-Raso, J. J. Fiol, E. Molins, P. Ballester, A. Frontera*, Cryst. Eng. Comm*, **2015**, DOI: 10.1039/C5CE01009H.

[11]. J. Adhikary, P. Chakraborty, S. Das, T. Chattopadhyay, A.Bauza, S. K. Chattopadhyay, B. Ghosh, F. A. Mautner, A. Frontera, D. Das, *Inorg. Chem.*, **2013**, 52, 13442-13452, dx.doi.org/10.1021/ic401819t

[12]. (a) M A.D. Becke, *Phys. Rev. A*, **1988**, 38, 3098. (b) C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B*, **1988**, 37, 785.

[13]. Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[14]. G. A. Zhurko; *Chem craft version* 1.7(build375) http://www.chemcraftprog.com

[15]. H. Tanak, A. E A. Agar, O. Buyukgungor, *Spectrochimica Acta Part A*, **2012**, 87, 15-24, doi:10.1016/j.saa.2011.10.055

[16]. B. S. Kusmariya, A.P. Mishra, *J Mol Struct.* , 2015, 1101, 176-188, http://dx.doi.org/10. 1016/j.molstruc.2015.08.026.

[17]. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination CompoundsPart B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry, Sixth Edition, *John Wiley & Sons, Inc., Hoboken, New Jersey*, **2009**, 210-222.

[18]. A. Carreño, M. Gacitua, D. P.Hernandez, R. Polanco, M. Preite, J. Fuentes, G. Mora, I. Chavez and R. A.Perez*, New J. Chem.*, **2015**, DOI: 10.1039/C5NJ01469G.

[19]. M. Klessinger, J. Michl, *Excited States and Photochemistry of Organic Molecules,* Chapter 2, **1995** VCH Publishers, New York, ISBN 1-56081-588-4, 63-135.

[20]. N. Raman, R. Mahalakshmi, T. Arun, S. Packianathan and R. Rajkumar, *J. Photochemistry and Photobiology B: Biology*, **2014**, 138**,** 211-222.

[21]. A. Taha , A. A. M. Farag, A. H. Ammarb, H. M. Ahmed *Spectrochimica Acta Part A*, **2014**, 130**,** 494-501.

[22]. R. K. Jain, A. P. Mishra, P. Gupta, *J Therm Anal Calorim,* **2012**, 110, 529-534, DOI 10. 1007/s10973-012-2401-8

[23]. R. K. Jain, A. P. Mishra, *J. Serb. Chem. Soc.,* **2012**, 77(8), 1013-1029, doi: 10.2298 /JSC111001023J

[24]. A.W. Coats and J. P.Redfern, *Nature*, **1964**, 201, 68-9.

[25]. H. H. Horowitz, G.Metzger, *Anal. Chem,* **1963**, 35, 1464-8.

[26]. N. T. Madhua, P. K. Radhakrishnan, M.Grunert, P. Weinberger, W. Linert, *Thermochim Acta,* **2003**, 400, 29–36

[27]. R. M. Issa, S. A. Amer, I. A. Mansour, A. I. Abdel-Monsef, *J. Therm. Anal. Calorim*, **2007**, 90, 261-267.

[28]. V. P. Singh, P. Singh, D. P. Singh, K. Tiwari, M. Mishra and A. Singh*, RSC Adv.*, **2015**, DOI: 10.1039/C4RA11929K.