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Cobalt(II) Bactericidal and Heat Resistant Complexes of ONS Donor Schiff Base Ligands: Synthesis and Combined DFT-Experimental Characterization

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Abstract

This paper reports the synthesis of four new tetra coordinate complexes of Cobalt(II) with Schiff base as a co-ligand of the composition $[Co(L^1)(L^2)]$ ·4H₂O where L¹ = N-(dehydroacetic acid)-thiosemicarbazide (tsc-dhaH₂), N-(dehydroacetic acid)-4-methyl-3-thiosemicarbazide (mtsc-dhaH₂), N-(dehydroacetic acid)-4-phenyl-3-thiosemicarbazide (ptsc-dhaH₂), or N-(dehydroacetic acid)-4-phenylsemicarbazide (psc-dhaH₂) and L² = benzimidazole, 2-aminobenzimidazole or 2-aminobenzithiozole. The nature of bonding and the stereochemistry of the complexes have been deduced from elemental analyses, conductivity measurements, magnetic susceptibility, mass spectrometry, thermogravimetric analysis, electrochemical, UV-Vis, infrared. The thermal decomposition processes of one of representative complexes are discussed and the order of reaction (*n*), the activation energies (*E_a*) have been calculated from thermogravimetric (TG) and differential thermogravimetric (DTG) curves. Molecular geometry optimizations, molecular surface electrostatic potentials (MESP), vibrational frequencies calculations, natural atomic charges and calculations of molecular energies, HOMO and LUMO were calculated for one of the representative Schiff base ligand (dha-pscH₂) and its respective complexes, [Co(dha-psc)(abtz)]·4H₂O from the Gaussian 09 software package by using density functional theory (DFT). Theoretical data have been found in an excellent agreement with the experimental results. Based on experimental and theoretical data, suitable square planar structure has been proposed for the present class of complexes. Moreover, a satisfactory antibacterial activity has been shown by the complexes.

Keywords: Cobalt(II) complexes; Spectroscopic techniques ; DFT Calculation; Antibacterial.

1. Introduction

Cobalt was accepted as an essential metal element widely distributed in the biological systems such as cells and body, and thus the interaction of DNA with cobalt complex has attracted much attention [1]. The biological role of cobalt is mainly focused on its presence in the active center of vitamin B_{12} , which regulates indirectly the synthesis of DNA. Additionally, cobalt is involved in the coenzyme of vitamin B_{12} used as a supplement of the vitamin [2]. Since the first reported studies into the biological activity of cobalt complexes [3], diverse structurally characterized cobalt complexes showing antitumor antiproliferative [4], antimicrobial [5], antifungal [6], antiviral [7] and antioxidant [8] activities have been reported. Schiff base ligands have been reported to show a variety of biological actions by virtue of the azomethine linkage, which is responsible for various antibacterial, antifungal, herbicidal, clinical and analytical activities [9–11]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest [12 14], because of their ability to possess unusual configuration. Derivatives of semicarbazone and thiosemicarbazone are amongst the most widely studied nitrogen and oxygen/sulphur donor ligands [15–18]. Particularly, thiosemicarbazone have emerged as an important class of sulphur donor ligands for transition metal ions because of their mixed hard–soft donor character and versatile coordination behaviour. In particular, transition

metal complexes of thiosemicarbazone have been receiving considerable interest largely because of their pharmacological property. Complexation of the thiosemicarbazone usually occurs via dissociation of the acidic proton, resulting in the formation of a fivemembered chelate ring. Such studies received a new impetus with the discovery of significant antibacterial, antiviral, antimalarial, antileprotic, and even anticancer activities of such ligands and some of their metal complexes, both in vitro and in vivo [19–25].

One of the oxygen heterocyclic compounds 3-acetyl-6methyl-2*H*-pyran- 2,4(3*H*)-dione (dehydroacetic acid or DHA) was reported to be an excellent chelating agent and to possess promising fungicidal, bactericidal, herbicidal and insecticidal activities [26-29]. It is also a versatile starting material for the synthesis of a wide heterocyclic ring svstems varietv of [30]. Dehydroacetic acid (dha) is biologically active compound and studies have shown that it has both antibiotic and antifungal effects [31, 32]. In aqueous solutions, it is a very strong antiseptic agent [33]. The compound is widely used in food technology, i.e., used to increase the stability of vitamin C and to protect vegetables during processing of food [34]. It is also used as preservatives in fish sausages [35].

Physiological activity and commercial applications of many benzimidazole derivatives have received much attention. Benzimidazole and its derivatives have different activities as they can act as bacteriostats or bactericides, fungicides, anti-carcinogens, etc [36-39]. This ring system is present in numerous antiparasitic, antihelmintics and anti-inflammatory drugs [40]. Several thousands of analogs of imidazole and benzimidazole have been synthesized and screened for pharmacological activity. Some of these compounds exhibited anti-HIV activity [41, 42]. The complexes of transition metals with benzimidazole and related ligands have been extensively studied as models of some important biological molecules [43-47].

Despite the recent increasing interest in thermogravimetric analysis for predicting thermal stabilities and estimating kinetic parameters, the thermal analysis techniques were extensively used in studying of the thermal behavior of metal complexes [48-50].

In order to understand the vibrational properties and structural characteristics of the ligand and complex, the density functional theory (DFT) calculation with B3LYP/6-311+G and LANL2MB combination has been carried out and the observed bands are assigned based on the results of normal coordinate analysis. To show the existence of intramolecular charge transfer (ICT) within molecular system energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels and the molecular electrostatic surface potential (MESP) energy surface studies are manipulated by DFT [51].

So, keeping in view the importance of Cobalt complexes and semicarbazone and thiosemicarbazone derivatives, we have undertaken the systematic study of the preparations, characterization of complexes of Co(II) with the Schiff ligands derived from condensation base of dehvdroacetic semicarbazone acid with and thiosemicarbazone derivatives. The structure of dehydroacetic acid, semicarbazone and thiosemicarbazone derivatives is shown in (Fig. 1).



Fig. 1. 2-D Structure of Organic Ligands used for the Synthesis of Schiff Bases.

2. Experimental

2.1. Materials, instruments and methods

Dehydroacetic Acid was the product of Merck Specialties Pvt., Ltd, Bombay, Semicarbazone and viz., thiosemicarbazone derivatives, Thiosemicarbazide, 4-phenyl-3-thiosemicarbazide, 4methyl-3-thiosemicarbazide, 4-phenyl-semicarbazide were products of Aldrich chemical Co., USA. Benzimidazole. 2-aminobenzimidazole. 2aminobenzithiozole were the products of Alpha Aesar, U.K. Cobalt(II) Sulphate heptahydrate was the product of B.D.H. Chemicals, Mumbai. ESI Mass spectra were recorded on a THERMO Finnigan LCQ advantage max ion trap mass spectrometer at SAIF, CDRI Lucknow. Solid-state infrared spectra were obtained using potassium bromide pellets with a Perkin-Elmer model FT-IR spectrophotometer, in our Department. Electronic studies were carried on UV-Visible-Near IR Spectrophotometer in our department. Conductance measurements were made in dimethylformamide solution using Toshniwal Conductivity Bridge and dip type cell with a smooth platinum electrode of cell constant 1.02. Magnetic susceptibility measurements were performed on Sherwood Scientific Magnetic Susceptibility Balance in our Department. Thermogravimetric analysis was done by heating the sample at the rate of 10 °C min⁻¹ from 25°C up to 1000°C on a thermal analyzer at SAIF, I.I.T., Bombay. Cyclic voltammetric measurements were carried out on Epsilon (Basi cell stand) electrochemistry system using a glassy carbon working electrode, platinum wire auxiliary electrode and an Ag/AgCl reference electrode. All solutions were purged with N₂ for 30 min before each experiment.

2.2. Preparation of Schiff bases

All the Schiff bases were prepared from the literature reported elsewhere [52].

(1) [dha-ptscH₂]

Yield 65%; mp 250 °C; FT-IR (KBr): 1616 (C=N), 817 (C=S), 3448 (OH), 1460 (C-O enolic), 3182 (N-H) cm⁻¹; Anal. Calcd for $C_{15}H_{15}N_3O_3S$: C= 56.77%, H= 4.76%, N= 13.24%. Found: C= 55.78%, H= 4.55%, N= 12.99%; MS-EI, $m/z = [M^+] = 318$.

(2) [dha-mtscH₂]

Yield 70%; mp 255 °C; FT-IR (KBr): 1618 (C=N), 820 (C=S), 3438 (OH), 1465 (C-O enolic), 3160 (N-H) cm⁻¹; Anal. Calcd for $C_{10}H_{13}N_3O_3S$: C= 47.05%, H= 5.13%, N= 16.46%. Found: C= 46.75%, H= 5.22%, N= 16.01; m/z = M⁺ = 256.

(3) [dha-pscH₂]

Yield 75%; mp 250 °C; FT-IR (KBr): 1604 (C=N), 3414 (OH), 1477 (C-O enolic), 3151 (N-H) cm⁻¹; Anal. Calcd for $C_{15}H_{15}N_3O_4$: C= 59.79%, H= 5.02%, N= 13.95%. Found: C= 58.66%, H= 5.05%, N= 12.21; m/z = M⁺ = 302.

(4) [dha-tscH₂]

Yield 75%; mp 250 °C; FT-IR (KBr): 1614 (C=N), 1589 (C=O acetyl), 1657 (C=O amide), 1262 (C-O enolic), 998 (V=O), 653 (V-O) cm⁻¹; Anal. Calcd for $C_9H_{11}N_3O_3S$: C= 44.80%, H= 4.60%, N= 17.42%. Found: C= 45.01%, H= 4.08%, N= 16.90; m/z = M⁺ = 242.

2.3. Synthesis of Cobalt(II) complexes

Cobalt sulphate heptahydrate (0.001 mol, 0.281 g) dissolved in ethanol (10 mL) by heating and the resulting solution was added to a warmed stirred solution of the corresponding Schiff base, dha-ptscH₂ (0.167 g, 0.001 mol) (1) or mtscH₂ (0.105 g, 0.001 mol) (2) or dha-pscH₂ (0.151g, 0.001 mol) (3) or dha-tscH₂ (0.091g, 0.001 mol) (4), in 15 mL of absolute ethanol. Monodentate ligand, viz., benzimidazole, 2-aminobenzimidazole, or 2-aminobenzithiozole was added to the mixture. The resulting solution was refluxed for 5–6 h when the desired compound separated out as a fine precipitate keeping the reaction mixture overnight. It was filtered by suction, washed several times with ethanol and then dried *in vacuo* over anhydrous calcium chloride.

(1c) [Co(dha-ptsc)(abzl)]·4H₂O

Yield 55%; mp 290 °C; FT-IR (KBr): 1604 (C=N), 1423 (C-O enolic), 781 (C-S), 3315 v(H₂O), 430 '(M-N), 1715 (C=O lactonic) cm⁻¹; UV-Vis (ethanol) (λ max, nm) (cm⁻¹): 230(43478), 284(35211), 384(26041); _M (⁻¹ cm² mol⁻¹): 13.2, μ_{eff} B.M.: 2.54; Anal. Calcd for C₂₂H₂₈CON₆O₇S: C= 45.60%, H= 4.87%, N= 14.50%. Found: C= 44.12%, H= 5.02%, N= 13.67; m/z = M⁺ = 580.

(2c) [Co(dha-mtsc)(bzl)]-4H₂O

Yield 60%; mp 280 °C; FT-IR (KBr): 1606 (C=N), 1420 (C-O enolic), 785 (C-S), 3314 v(H₂O), 433 '(M-N), 1717 (C=O lactonic) cm⁻¹; UV-Vis (ethanol) (λ max, nm) (cm⁻¹): 255(39215), 285(35087), 359(27855); _M (⁻¹ cm² mol⁻¹): 13.9, μ_{eff} B.M.: 2.65; Anal. Calcd for C₁₇H₂₅CoN₅O₇S: C= 40.64%, H= 5.02%, N= 13.94%. Found: C= 38.27%, H= 4.11%, N= 12.22; m/z = M⁺ = 503.

(3c) [Co(dha-psc)(abtz)]-4H₂O

Yield 55%; mp 285 °C; FT-IR (KBr): 1597 (C=N), 1429 (C-O enolic), 3408 (H₂O), 418 v(M-N), 1712 (C=O lactonic) cm⁻¹; UV-Vis (ethanol) (λ max, nm) (cm⁻¹): 257(38910), 287(34843), 356(28089); M (⁻¹ cm² mol⁻¹): 14.1, μ_{eff} B.M.: 2.92; Anal. Calcd for C₂₂H₂₇CoN₅O₈S: C= 45.52%, H= 4.69%, N= 12.06%. Found: C= 45.02%, H= 4.32%, N= 11.05; m/z = M⁺ = 579.

(4c) [Co(dha-tsc)(bzl)]-4H₂O

Yield 75%; mp 250 °C; FT-IR (KBr): 1599 (C=N), 1425 (C-O enolic), 788 (C-S), 3410 v(H₂O), 441 '(M-N), 1712 (C=O lactonic) cm⁻¹; UV-Vis (ethanol) (λ max, nm) (cm⁻¹): 230(43478), 284(35211), 364(27472); M (⁻¹ cm² mol⁻¹): 14.6, μ_{eff} B.M.: 2.55; Anal. Calcd for C₁₆H₂₃CoN₅O₇S: C= 39.35%, H= 4.75%, N= 14.34%. Found: C= 37.35%, H= 3.98%, N= 13.22; m/z = M⁺ = 489.

2.4. Screening of Antibacterial Activities

The in vitro biological screening effects of the investigated compounds were tested against gram negative bacteria Escherichia coli, MTCC 1304 at different concentrations by the well diffusion method using agar nutrient as the medium. Mueller Hinton agar plates (MHA) were prepared and 50 µL Escherichia suspensions of coli containing approximately 10⁵ CFU (colony forming unit) were applied to the plate by the well diffusion method [53]. The wells were made on the plates and they were filled with 50 µL of sample solution of 0.02 % 0.02 % concentration. The solution of Chloramphenicol was used for comparison. These plates were incubated at 37±1 °C for 24 - 48 h in refrigerated incubator shakers.

2.5. Computational Methods

In order to understand the vibrational properties and structural characteristics of the ligands and complexes the density functional theory (DFT) calculation with B3LYP/6-311+G and B3LYP/LANL2MB combinations have been used respectively and the observed bands are assigned based on the results of normal coordinate analysis. By combining the results of the GAUSSVIEW program [54] with symmetry considerations along with available related molecules, vibrational frequency assignments were made with a high degree of accuracy.

With the aim to obtain a deeper understanding of the interaction between cobalt ion and ONS environment, *ab initio* total energy calculations within the density functional theory (DFT) frame work were carried out for dha-pscH₂ ligand and one of the representative synthesized complex [Co(dha-psc)(abtz)]·4H₂O. The optimized structures, vibrational frequencies, HOMO-LUMO, MESP, Mulliken charges and NBO charges are presented and discussed. All the theoretical calculations manifested by Gaussian 09 software package [55] were performed at the Department of P. G. Studies and Research in Chemistry and Pharmacy R. D. University Jabalpur, M. P.

3. Results and Discussion

The Schiff base ligands used in the present study were prepared from dehydroacetic acid and semicarbazide or thiosemicarbazide derivatives as shown in **Fig. 2**.



Fig. 2. Synthesis of Schiff bases.

The formation of Schiff base is consistent with the micro analytical data of the ligand and is confirmed by the appearance of the azomethine peak at 1604-1618 cm^{-1} in the infrared spectra of all the ligands.

The Cobalt(II) complexes were prepared as per the reaction given below.

$$CoSO_4.7H_2O + L^1H_2 + L^2 \xrightarrow{\text{Ethanol, H}_2O} [Co(L^1)(L^2)] \cdot 4H_2O + 3H_2O + H_2SO_4$$

Where $L^{1}H_{2} = dha-ptscH_{2}$, $dha-mtscH_{2}$, $dha-pscH_{2}$ or $dha-tscH_{2}$

 $L^2 = bzl$, abtz or abzl

These complexes are found to be thermally stable and are insoluble in most of the common organic solvents but are fairly soluble in DMF, DMSO and Acetonitrile. The formulation of these complexes is based on their Physico-chemical and theoretical studies. The proposed structure of complexes is shown Scheme I.





3.1. Conductance measurements

The observed molar conductance (13.2–14.6 ohm⁻¹cm² mol⁻¹) in 10⁻³ molar DMSO solutions indicates non-electrolytic nature of the complexes. Such a non-zero molar conductance value for each complex in the present study is most probably due to the strong donor capacity of DMF, which may lead to the displacement of anionic ligand and change of electrolyte type [56].

3.2. Magnetic measurements

The observed magnetic moments of all synthesized complexes depicts that all the complexes show magnetic moments in the range of 2.54 – 2.92 B.M, indicating square-planar configuration [57].

3.3. Infrared Spectral Studies

All the ligands used in the present investigation exist in enol and thiol form (vide supra) as shown in (Fig. 3).

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They possess several potential donor sites: three hydrazinic nitrogens Ν₁, N_2 and N₄ of thiosemicarbazide moiety, thione/thiolic sulphur, enolic oxygen of dhaH and pyran carbonyl oxygen of DHA. Considering the planarity of the ligands, the coordination of pyran C=O oxygen is unlikely due to being back side of the suitable donor sites. It has also been confirmed by looking at the persistence of 1712 cm⁻¹ peak both in ligand and the complex. Moreover, the coordination of the N_2 and N_4 will be less favored in presence of neighbouring azomethine nitrogen, N₁ and thiol-S/enol-O which will form 5-membered chelate ring including central metal after complexation. Both N-N and N-H frequencies remained unaltered on complexation and hence proves their inertness towards coordination to metal as revealed by no change in v(N-N) (950–960 cm⁻¹) and v(N-H) (3155-3182 cm⁻¹) of the free ligands after complexation.

The IR spectrum of all ligands showed a sharp band at 1604-1618 cm⁻¹ corresponding to vC=N azomethine group. In the IR spectra of all the complexes, this band has observed to low energy shift at 1597-1606 cm⁻¹ indicating the coordination of azomethine nitrogen atom [58]. The ligand (1), (2) and (4) displays v(C=S) absorptions at 817, 820 and 815 cm⁻¹ respectively and were disappeared upon complexation. These observations may be attributed to the enolization of – NH–C=S and subsequent coordination through the deprotonated sulfur [59]. However, such coordination is supported by the shifting of the (C-S) band to lower

wave number at 781, 785, 788 cm⁻¹ in the complexes (1c), (2c) and (4c) respectively.

The characteristic enolic (OH) mode in all the ligands due to the presence of an hydroxyl group was observed at 3414- 3448 cm⁻¹. A medium band at 1460-1477 cm^{-1} due to (C-O) of the enolic group was also observed in these ligands. The band due to enolic (OH) of these ligands was found be absent in all of the complexes under study to indicate the coordination of the enolic oxygen, after deprotonation, to the metal ion. However, such coordination is supported by the shifting of the enolic (C-O) band to lower wave number at 1420-1429 cm⁻¹ in the complexes. The presence of lattice water in the all compounds is revealed by the absorption of weak band at 3408-3415 cm⁻¹. An absorption band observed at 636 cm⁻¹ is due C-S-C group of 2-aminobenzithiozole moiety coordinated to complex (3c). However the appearance of sharp bands in compounds (1c) and (3c) at 3261-3277 cm⁻¹ are due to $-NH_2$ group of derivatives of imidazole moiety coordinated to metal ion. The appearances of new bands at 418- 441 cm⁻¹ are due to the v(M-N).

The experimental IR spectra of Schiff base ligands $(psc-dhaH_2)$ and its complex $[Co(psc-dha)(abtz)]\cdot 4H_2O$ are given in **Fig. 4 and Fig. 5** respectively. Moreover, DFT computational IR spectrum also shows almost close resemblance with the important spectral bands with that of corresponding experimental spectral bands as shown in (**Fig. 6**).









Fig. 5. I. R. Spectra of Complex [Co(psc-dha)(abtz)]·4H₂O (3c)

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Fig. 6. IR spectra of Complex [Co(psc-dha)(abtz)]·4H₂O (3c) , (a) Experimental (b) Theoretical.

3.4. UV-Vis Studies

The electronic spectrum of compound (3c) in 10^{-3} M DMSO solutions was recorded in the range 200-800 nm.

The electronic spectrum of compound exhibits four absorption peaks. The three high intensity peaks in the

UV region appearing at 38910 cm⁻¹, 34843 cm⁻¹ and 28089 are due to relatively higher intensities ligand metal charge transfer transitions. The fourth broad peak at 21052 cm⁻¹ is due to ${}^{1}A_{1g}$ ${}^{1}B_{1g}$ transition suggesting a true square planar geometry [60] for this complex. This is further confirmed by its magnetic susceptibility value (2.92 B.M).



Fig. 7. Electronic Spectrum of complex [Co(psc-dha)(abtz)]·4H₂O (3c).

3.5. Thermal analysis

Thermogravimetric analyses of one of the representative compounds, $[Co(dha-psc)(abtz]\cdot4H_2O(3c) was carried out ($ **Fig. 8**) in the temperature range of 30–1000 °C at the heating rate of 10 °C/min. The compound showed a weight loss of 13.33 % at 30–100°C, which corresponds to the elimination of four molecules of lattice water (calculated weight loss = 12.41 %). The compound shows another weight loss

of 22.94 % at 100–360 °C, which corresponds to the removal of 2-aminobenzithiozole moiety (calculated weight loss = 25.85). The thermogram showed one more weight loss in the temperature range of 360–715°C (observed 44.75 %) assuming the elimination of Schiff base ligand moiety (dha-pscH₂) (calcd. 51.08 %,). The final residue attaining a constant weight (observed 18.97%) over 715 °C roughly corresponds to CoO (calcd. 14.12 %). These results are consistent with IR results for this complex.



Fig. 8. TG Curve of Complex [Co(psc-dha)(abtz)]·4H₂O (3c).

3.6. Thermodynamic Studies based on TGA Spectra

In the present studies of the metal complexes, nonisothermal mode for TGA/DTA techniques is selected for one representative complex [Co(dhapsc)(abtz)]·4H₂O (**3c**). From Broido graphical method and Broido plots [61] (**Fig. 9**) the activation energy and order at a particular Step (I), Step (II) and Step (III) are calculated and the results are given in Tables **1(a**, **b)**. The order 'n' is calculated by the application of Horowitz-Metzger equation [62] as given below

$$C_s = n^{4/(1-n)}$$
(i)
 $C_s = \frac{W_t - W_a}{W_0 - W_a}$ (ii)

Where, C_s is the mass fraction of the substance.



Fig. 9. Broido plots of Complex [Co(dha-psc)(abtz)]·4H₂O (3c).

Int. J. Curr. Res. Chem. Pharm. Sci. (2016). 3(4): 50-72 Table 1(a) Thermal behavior and thermodynamic parameters of [Co(dha-psc)(abtz)]·4H₂O (3) complex.

				Step I			
Temp. °	C	Temp K	1/K X 10 ³	Residue %	W _t	$C_s = W_t - W_a$ $W_o - W_a$	1/ C _s
62		335	2.985	99.32	1.1799	0.991	1.009
72		345	2.898	99.25	1.1790	0.990	1.010
82		355	2.816	96.95	1.1517	0.962	1.039
92		365	2.739	93.28	1.1081	0.917	1.090
102		375	2.666	86.56	1.0246	0.830	1.204
112		385	2.597	86.25	1.0246	0.830	1.204
122		395	2.531	85.95	1.0210	0.826	1.210
132		405	2.469	85.34	1.0138	0.819	1.221
				Step II			
Temp.	°C	Temp K	1/K X 10 ³	Residue %	W _t	$\frac{C_s = W_t - W_a}{W_o - W_a}$	$1/C_{s}$
200		473	2.114	84.72	1.0064	0.811	1.233
210		483	2.070	83.81	0.9956	0.800	1.250
220		493	2.028	83.32	0.9898	0.794	1.259
230		503	1.988	82.28	0.9774	0.781	1.280
240		513	1.949	81.06	0.9629	0.766	1.305
250		523	1.912	74.95	0.8379	0.636	1.572
260		533	1.876	66.40	0.7888	0.585	1.709
270		543	1.841	60.90	0.7234	0.517	1.934
				Step III			
Temp. °	°C	Temp K	1/K X 10 ³	Residue %	W _t	$C_s = W_t - W_a$ $W_o - W_a$	1/ C _s
450		723	1.383	40.12	0.4766	0.261	3.831
460		733	1.364	37.07	0.4403	0.223	4.484
470		743	1.345	36.46	0.4331	0.216	4.629
480		753	1.328	35.23	0.4185	0.200	5.000
490		763	1.310	34.01	0.4040	0.185	5.405
500		773	1.293	32.18	0.3822	0.163	6.134
510		783	1.277	31.57	0.3750	0.155	6.451
520		793	1.261	30.35	0.3605	0.140	7.142
				Table 1(b)			
mplex	Step		Step analysis	°C	$C_s = W_t - W_t$	/ _a Order	E_(K
1		Ti	T _{max}	Τ _f	vv _o -vv _a	(n)	-a(· ·
uctural rmula	Ι	335	375	405	0.991	x	132.5
	П	473	513	543	0.811	4	63.1

 T_i = Initial Temperature; T_{max} = Maximum Temperature; T_f = Final Temperature.

0.261

793

3.7. Electrochemical Properties

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Cyclic voltammetric measurements of one of the representative complex $[Co(dha-psc)(abtz)]\cdot 4H_2O$, was carried out on an ECDA-001 basic electrochemistry system in order to assess the suitability of ligand environments in the present

723

763

complex to facilitate electron transfer reactions. The complex was dissolved in DMSO and the cyclic voltammogram was recorded in the scan range of +1500 to -1500 mV in the presence of 0.1 M of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte.

1

56.38

The Co(II) complex exhibited one electron quasi reversible transfer process with a reduction peak at

 E_{pc} = -448 mV with a corresponding oxidation peak at E_{pa} = -270 mV at a scan rate of 100mV/s (**Fig. 10**).





The peak separation (ΔE_p) of this couple is 178 mV. With the increasing scan rates, (ΔE_p) value also increases giving further evidence for the quasireversible Co(II)/Co(I) couple [63] Table 2. The difference between forward and backward peak potentials can provide a rough evaluation of the degree of the reversibility. The ratio of cathodic to anodic peak height was less than one. However, the peak current increases with the increase of the square root of the scan rates. This establishes the electrode process as diffusion controlled.

Complex	Couple	Scan Rate mV/sec	<i>E</i> _{pc} (mV)	<i>E</i> _{pa} (mV)	E _r (mV)	∆ <i>E</i> (mV)	i _{ρc} (μΑ)	i _{pa} (μΑ)
[Co(dha-psc)(abtz)]4·H ₂ O	Co(II)/Co(I)	100	-448	-270	-359	178	24.33	-3.75
		200	-486.9	-267	-377	219	43.27	-10.71
		300	-518.3	-243.5	-381	274.8	61.11	-18.45
		500	-581.2	-188.5	-384	392.7	98.89	-37.02

3.8.Computational Studies 3.8.1. Geometrical Parameters

The various bond lengths, bond angles and dihedral angles generated from the optimized structure of one of the representative complexes, [Co(dha-psc)(abtz)]·4H₂O using Gaussian 09 software are given in the Table 7. The optimized geometry of both the model compounds furnished the total energy E (RB3LYP), -1032.31 a. u. or -28091 eV for ligand, where as -1561.54 a. u. or -42492.62 eV was the result obtained for the coordination complex. The

computed bond lengths, such as, Co-O(10), Co-O(15), Co-N(26) and Co-N(12) in the present complex are 1.781, 1.821, 2.005 and 1.862 Å respectively. The significant computed bond angles in the complex, such as, O(10)-Co(23)-N(12), (93.94°), N(26)-Co(23)-O(15), (89.46°), N(26)-Co(23)-O(10), (89.79°), O(15)-Co(23)-N(12), (86.73°), O(10)-Co(23)-O(15), (170.40°), N(12)-Co(23)-N(26), (176.20°) suggest the square planer structure of the present as well as the other complexes in question. The Optimized structure of complex [Co(dha-psc)(abtz)]·4H₂O (**3c**) is shown in (**Fig. 11**).

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Fig. 11. Optimized Structure of complex [Co(dha-psc)(abtz)]·4H₂O (3c)

3.8.2. Frontier Molecular Orbitals Analysis

HOMO and LUMO are very important parameters [64] for chemical reaction. One can determine the way the molecule interacts with other species. Hence, they are called the Frontier orbitals. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor, and the gap between HOMO and LUMO characterizes the molecular chemical stability [65]. Four important molecular orbitals (MOs) namely, second highest [HOMO-1], and highest occupied MO's [HOMO], the lowest [LUMO], second lowest [LUMO+1] have been worked out for ligand dha-pscH₂. The computed energies of these four molecular orbitals observed for a ligand [dha-pscH₂] are: -4.0469, -2.6977, 0.6424 and 2.0828 eV respectively, and the energy gap (ΔE) between their [HOMO- LUMO], [HOMO-1 - LUMO+1] is 3.340 and 6.1297 eV, respectively. Similarly four

(MO's), are worked out for the complex, [Co(dhapsc)(abtz)]·4H₂O (**3c**) and the observed energies in the same order are as -4.2624, -3.8780, 0.0734, and 0.2674 eV, while the energy gap between [HOMO-LUMO] and [HOMO-1-LUMO+1] are 3.9464 and 4.5298 eV, respectively. The electronic fillings of MO's in (dha-pscH₂) indicates diamagnetic nature while as its complex [Co(dha-psc)(abtz)]·4H₂O verifies that it is paramagnetic.

The energy of the frontier orbitals for molecules in term of ionization energy (IE) and electron affinity (IA) of the (dha-pscH₂) and its complex from Koopmans's theorem [66] is:

-E_{HOMO} =IE,(iii)

-E_{LUMO} = EA(iv)

The absolute electronegativity (χ_{abs}) and absolute hardness (η) are related to IA and EA [67] as given below:

$$\chi_{abs} = (IE + IA)/2 = (E_{HOMO} + E_{LUMO}) / 2$$
(v)
 $\eta = (IE - IA)/2 = (E_{HOMO} - E_{LUMO}) / 2$ (vi)

A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity and low kinetic stability and is also termed as soft molecule while as hard molecules have a large HOMO-LUMO gap [68]. The absolute electronegativity (χ_{abs}), absolute hardness (η) of [dhapscH₂] and its complex calculated using equations (v) and (vi) are represent in Table 3. The energy gap between HOMO and LUMO in complex as compared to ligands is a key factor to mark the stability difference between the two. The HOMO–LUMO structures with energy level diagram of (dha-pscH₂) and its complex are shown in **Fig. 12 and Fig. 13** respectively.



Fig. 12. HOMO-LOMO structure with energy level diagram of (psc-dhaH₂) ligand.



Fig. 13. HOMO-LOMO structure with energy level diagram of [Co(psc-dha)(abtz)]-4H₂O (3c) complex.

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Another important property related to the dipole	ω = μ2/2η	(vii)
moment and hardness is electrophilicity index (ω),	S = 1/η	(viii)
global softness (S) shown in below equation. The		
values of ω and S are given in (Table 3).		

Table 3. Absolute electronegativity (χ_{abs}) and absolute hardness (η) electrophilicity index (ω), global softness (S) of[dha-pscH2] and its complex [Co(dha-psc)(abtz)]·4H2O (**3c**).

Compounds	χ _{abs} (eV)	η (eV)	ω (Debye/eV)	S (eV)	µ (Debye)
[dha-pscH ₂]	-1.027	-1.6700	-4.964	-0.5988	4.0730
[Co(dha-psc)(abtz)]5H ₂ O	-1.899	-3.946	-0.867	-0.253	2.6162

3.8.3. Hyperpolarizability Calculations

The density functional theory has been used to calculate the dipole moment (~), mean polarizability

(r) and the total first static Hyperpolarizability (s₀) for compound [Co(dha-psc)(abtz)]·4H₂O (**3c**) in terms of x, y, z components and their values (a.u) are given in Table **4** [69,70].

Table 4. Cal	culated all (μ, β, α) compone	nts and (μ, β, α	α)-total of complex	[Co(dha-psc)	(abtz)]⋅4H ₂ O ∉	(3c)
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Di	pole moment (~)		Hyperpolarizability (s)		
μ _x	-2.2440	β _{xxx}	-51.10		
μ _v	0.9606	β _{ννν}	12.44		
μ _z	0.9412	β _{zzz}	-1.49		
μ_{total} .	2.6161	β _{xyy} -43.65			
Ро	larizability(r)	β _{xxv}	71.49		
α _{xx}	-172.86	β _{xxz}	47.22		
ανν	-191.69	β_{xzz}	-20.72		
α _{zz}	-195.54	β _{yzz}	-23.09		
α _{xy}	-12.76	β _{yyz}	-12.62		
α _{xz}	1.56	β_{xvz}	-13.50		
α _{vz}	-8.52	β ₀	134.65		
α total	-184.01				
Δα	21.02				

Where α_{xx} , α_{yy} and α_{zz} are tensor components of polarizability: β_{iiz} , β_{izi} and β_{zii} (i from x to z) are tensor components of hyperpolarizability: μ_x , μ_y and μ_z are the components of the dipole moment. α is the mean polarizability, $\Delta \alpha$ is the anisotropy of polarizability, β_0 is the mean first hyperpolarizability.

3.8.4. Atomic Net Charges

The natural atomic charges of a representative complex, $[Co(dha-psc)(abtz)]\cdot 4H_2O$ (**3c**) obtained by NBO and Mulliken population analysis [71] with B3LYP/ LANL2MB basis set are compared in Table **5**. The comparison between Mulliken's net charges and the atomic natural ones is not an easy task since the

theoretical background of the two methods was very different. Looking at the results there are surprising differences between the Mulliken's and the NBO charges. The observation of the data given in the table indicates that the atoms namely C_1 , C_3 , C_5 , C_7 , C_{14} , C_{17} , C_{25} , C_{27} , C_{25} and all hydrogen bear positive charge both in NBO and Mulliken analyses. The Co_{23} also bears positive charge in Mulliken analysis while as negative charge in NBO analysis. The remaining atoms bear negatively charges over them in both the analysis. The color range in the scale of positive and negative charge (a) NBO atomic charges and (b) Mulliken atomic charges of the complex is shown in (**Fig. 14**).



Fig. 14. Structure of with color range (a) Mulliken atomic charges (b) NBO atomic charges of [Co(dha-psc)(abtz)]·4H₂O (**3c**)

The Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system because of atomic charges effect dipole moment, molecular polarizability, electronic structure, and a lot of properties of molecular systems. The definition of Mulliken's charges is based on population analysis. The Mulliken population analysis provides a partitioning of either the total charge density or an orbital density. The number of the electrons in the molecule (N) is the integral of the charge density over the space. N is partitioned for all atoms considering also the overlap population. According to the theory the overlap population of atoms A and B is divided between the two atoms in half-to-half ratio. This is one weak point of the theory. The other weak point is its strong dependence on the basis set applied. The atomic net charge is the difference between the calculated number of electrons belonging to the atom in the complex and the number of electrons of the isolated atom.

The natural atomic charge is based on the theory of the natural population analysis. The analysis is carried out with natural bond orbitals (NBO). They are linear combinations of the natural atomic orbitals. The derivation of a valence-shell atomic orbital (NAO) involves diagonalization of the localized block of the full density matrix of a given molecule associated with basis functions on that atom. A distinguishing feature of NAOs is that they meet the simultaneous requirement of orthonormality and maximum occupancy. In a polyatomic molecule the NAOs mostly retain one-center character, and thus they are optimal for describing the molecular electron density around each atomic center. Natural bond orbitals are linear combinations of the NAOs of two bonded atoms. The natural population analysis satisfies Pauli's exclusion principle and solves the basis set dependence problem of the Mulliken's population analysis [72].

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S. No.	Atom With the Numerical Assignment	NBO Partial Charges	Mulliken Partial Charges	S. No.	Atom With the Numerical Assignment	NBO Partial Charges	Mulliken Partial Charges
1	1 C	0.1753	0.1179	28	28 C	0.0567	0.0083
2	2 C	-0.1557	-0.0734	29	29 C	-0.0518	-0.0713
3	3 C	0.2874	0.2111	30	30 C	-0.0467	-0.0745
4	4 O	-0.2283	-0.1980	31	31 C	-0.0495	-0.0754
5	5 C	0.2164	0.1316	32	32 C	-0.0617	-0.0683
6	6 C	-0.1683	-0.1230	33	33 N	-0.3770	-0.3555
7	7 C	0.1976	0.1188	34	34 H	0.0772	0.1015
8	8 C	-0.2061	-0.2254	35	35 H	0.0772	0.0954
9	9 O	-0.1535	-0.1418	36	36 H	0.0821	0.0993
10	10 O	-0.1818	-0.1749	37	37 H	0.0817	0.0989
11	11 C	-0.2296	-0.2492	38	38 H	0.1086	0.1274
12	12 N	-0.1162	-0.1585	39	39 H	0.0694	0.0832
13	13 N	-0.1838	-0.1964	40	40 H	0.0831	0.0986
14	14 C	0.3206	0.2509	41	41 H	0.2056	0.2162
15	15 O	-0.2534	-0.2327	42	42 H	0.0609	0.0882
16	16 N	-0.2694	-0.2531	43	43 H	0.0551	0.0829
17	17 C	0.0838	0.0584	44	44 H	0.0528	0.0805
18	18 C	-0.0783	-0.0921	45	45 H	0.0541	0.0820
19	19 C	-0.0510	-0.0795	46	46 H	0.0594	0.0879
20	20 C	-0.0571	-0.0832	47	47 H	0.0816	0.1068
21	21 C	-0.0501	-0.0784	48	48 H	0.0587	0.0870
22	22 C	-0.0655	-0.0793	49	49 H	0.0592	0.0876
23	23 Co	-0.0990	0.0857	50	50 H	0.0730	0.1012
24	24 S	-0.2362	-0.2016	51	51 H	0.2304	0.2314
25	25 C	0.3333	0.2286	52	52 H	0.2780	0.2671
26	26 N	-0.2533	-0.2399				
27	27 C	0.1040	0.0908				

Table 5. Representation data of Mulliken atomic charges and NBO analysis of [Co(dha- psc)](abtz)]·4H₂O (3c).

3.8.5. Molecular Electrostatic Potential (MESP) of Ligand and its Complex

The molecular electrostatic potential (MESP) is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions [73,74].

The molecular electrostatic potential, V(r), at a given point r(x, y, z) in the vicinity of a molecule is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at

r. For the system studied, the V(r) values were calculated as described previously using the following equation [75]

where Z_A is the charge of nucleus A located at R_A , $\rho(r')$ is the electronic density function of the molecule, and r' is the dummy integration variable. Being a real physical property, V(r)can be determined experimentally by diffraction or by computational methods [76]. To predict reactive sites for electrophilic and nucleophilic attack for the title molecule, MESP was calculated at the 6-311G(+) and LANL2MB optimized geometries. The negative (red) regions of MESP were related to nucleophilic reactivity and the positive (blue) regions to electrophilic reactivity shown in (Fig. 15).



Fig. 15. Molecular electrostatic potential MESP (a) [dha-pscH₂] and (b) [Co(psc-dha)(abtz)]·4H₂O (**3c**) with colour range along with Scale.

As can be seen from figure the MESP map of a ligand (dha-pscH₂) shows that the imine group and hydroxyl oxygen atoms represent the most negative potential region, while in the case of the complex the coordination environment of ON and oxygen (lactonic) is the region of most negative potential. The hydrogen atoms in a ligand (dha-pscH₂) bear the region of maximum positive charge. Moreover almost all hydrogens are present in electrophilic regions. The predominance of green region in the MESP surfaces corresponds to a potential halfway between the two extremes red and dark blue color.

3.9. Antibacterial Screening

Antibacterial activity of the ligands and its complexes has been carried out against bacteria, *E. coli*, using

nutrient agar medium by the well diffusion method [53]. The results in the form of zone inhibition were measured in mm. It was observed that all metal complexes show much more activity in comparison to Schiff base, probably due to the enhanced lipophilicity of the complexes, which leads to the breakdown of permeability barrier of the cell and thus retards the normal cell process in bacteria. It is postulated that improved activity arises from the delocalization of positive charge between the organic moiety and the metal, which favours the drug entering into normal cellular processes of the bacteria. The complexes **1c**, **2c**, **3c** and **4c** are most potent complexes which have inhibition almost equal to antibiotic.

S. No	Ligand/Complex	Activity against <i>E. coli</i>	*Inhibition Zone in mm
1	(ptsc-dhaH ₂)	+	14
1c.	[Co(dha-ptsc)(abzl)]⋅4H₂O	+	20
2 2c.	(mtsc-dhaH₂) [Co(dha-mtsc)(bzl)]·4H₂O	+ +	16 27
3 3c.	(psc-dhaH₂) [Co(dha-psc)(abtz)]∙4H₂O	+ +	13 34
4 4c.	(tsc-dhaH₂) [Co(dha-tsc)(abzl)]⋅4H₂O	+ +	17 21
	Chloramphenicol	+	37

Table 6. Antibacterial screening activity against E.coli.

*Diameter of inhibition zone >8mm is taken as active and is shown as + in the table.





Fig. 16. Inhibition Zone in (a) Schiff base (psc-dhaH₂) 3 and (b) Complex [Co(dha-psc)(abtz)]·4H₂O (3c).

The increased activity of metal complexes can be explained on the basis of 'Overtone's concept' and 'Chelation theory'. According to 'Overtone's concept' of cell permeability the lipid membrane that surrounds the cell favors the passage of only lipid soluble materials due to which liposolubility is an important factor which control the antimicrobial activity. On Chelation, the polarity of metal ion will reduce to a greater extent due to overlap of the ligand and metal orbital and partial sharing of positive charge of the metal ion with donor groups. Further, it increases the delocalization of -electrons over the whole chelate ring enhanced the lipophilicity of the complexes into lipid membrane and blocks the metal binding sites on enzyme of pathogenic microorganism. The detail result of antibacterial screening for 0.02 % concentration is given in Table 6 and the photographs

of antibacterial screening result showing zone of inhibition are presented in **Fig. 16(a, b).**

4. Conclusion

On the basis of Physico chemical and computational studies discussed above, square planar geometry for Co(II) complexes are proposed. The ligands behave as tridentate, coordinating through carbonyl oxygen, imino nitrogen and thiolic sulphur. The thermal study of compound (3c) shows that the complex is thermally stable. Scheme I shows the proposed structure of complexes. Thermal behavior studied so far unravel the fact that the complex is stable up to considerable temperature. The agreement between experimental and theoretical outcomes is stemming the assumption made at various steps in structural elucidation.

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