



Synthetic Approach, Structural Performance and *in vitro* Antibacterial Activity: Nitrogen and Oxygen Donor Atoms containing Bidentate Schiff Base Ligand and its Mononuclear Complexation with Co(II) and Cu(II) Metal Ions

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A synthetic approach has been designed and followed for the synthesis of new bidentate Schiff base ligand 2-acetylthiophenecotinic hydrazone (L) (which possessed nitrogen and oxygen donor atoms) and its Co(II) and Cu(II) mononuclear complexes. All the compounds were examined IR, ¹H NMR, mass, EPR, conductivity, elemental analysis, etc. Octahedral geometry has been assigned to all synthesized compounds on the basis of magnetic, IR and electronic spectral analysis. *In vitro* activity i.e. antibacterial (*E. coli* and *P. aeruginosa*) and antifungal (*A. niger*, *M. phasolina* and *P. glomerata*) had been examined for these compounds following well diffusion and poisoned food methods, respectively. During the performance of antifungal activity, antifungal agent was incorporated into the molten agar at various concentrations and mixed well. After performance of *in vitro* activity, it has been resulted out that metal(II) complexes exhibited remarkable activity than free ligand but less active compared to the standard drugs..

Keywords: Schiff base, Acetylthiophenecotinic hydrazone, Metal(II) complex, Well diffusion method, Poisoned food method.

INTRODUCTION

Coordination chemistry is one of the important branch of chemistry and one of the most active research areas from the past decades to till now [1-3]. In the field of coordination chemistry in 1913, for the pioneering contribution of Werner, he received Nobel Prize [4]. From the time of Werner & Jorgenson, attentions of researchers have been increased in the field of coordination chemistry [5-8]. In this area, there has been growing awareness and interest to study the role of a wide range of organic molecules such as Schiff base ligands which contain nitrogen, oxygen and sulphur donor atoms and inorganic elements such as transition metal ions [9-12]. Some specifications like ease of use, a range of variety and structural variability make Schiff bases and their metal complexes are highly valuable [13,14]. The chelating process which involves binding of a ligand to a metal ion through two or more donor atoms (nitrogen, oxygen and sulphur) is a

versatile method to realize this and may be present in different combination of donor atoms [15,16].

Assembly of metal-organic framework (i.e. ligand metal complexation) with various network topologies had been prepared from the metal-organic building block [17]. The applications of these synthesized ligands and complexes have been highly explored in inorganic, organic and biological fields [18-22]. Additionally, bidentate Schiff base ligands which possessed N,O-donor atoms in their framework are well known and applicable for the formation of their mononuclear complexes and also screened for their significance biological applications [23-27]. Usually, N,O-donor Schiff bases can be derived by condensing the aldehydes or ketones with varied primary amines/amino acids [28-30]. From a long time, the organic frame work for N and O donor atoms containing ligands had been prepared by use of nicotinic hydrazide as an amine moiety [31,32]. Synthesized Schiff base ligands are their metal complexes considered on a

large scale because of their well-known application in biological fields *i.e.* antiviral, antioxidant, antibacterial, antifungal, anticancerogenic and antitumor, anti-inflammatory, antimalarial, DNA binding and cleavage *etc.* [33-35]. In this work, synthetic approach for mononuclear cobalt(II) and copper(II) complexes of acetylthiophenenicotinic hydrazone ligand has been studied. Ligand has been derived from nicotinic hydrazide and 2-acetylthiophene in 1:1 ratio in ethanolic medium and its metal complexes also synthesized by condensation reaction. *In vitro* biological screening of synthesized ligand and its metal complexes has been also done for consideration of their antibacterial and antifungal activities.

EXPERIMENTAL

All the AR grade chemicals have been used for the completion of this research work. Procured solvents have been used as received. By using Carlo-Erba 1106 Elemental Analyzer has been used for analyzing presence of elements (carbon, hydrogen and nitrogen). BX-II spectrophotometer was used for recording infrared spectra of synthesized compounds in form of KBr pellet in the range of 4000-400 cm^{-1} and UV-visible spectra was analyzed by using DMSO solvent on Shimadzu UV-visible mini-1240 spectrophotometer. Magnetic properties of synthesized complexes has been analyzed by using Gouy Balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at room temperature. Electron paramagnetic resonance spectra were recorded at room temperature on spectrophotometer named E4-EPR at SAIF, IIT Bombay, India. Spectrophotometer Bruker Advanced DPX-300 was used for recording proton NMR spectrum of ligand at IIT, Delhi. JEOL, JMS-DX-303 spectrophotometer was used for recording mass spectrum. Hyperchem. 7.51 version has been used to carry out computational studies for synthesized compounds.

Molecular modeling: To obtain the structural information of synthesized ligand and its metal(II) complexes, the computational work *i.e.* molecular modeling has been performed. By using Hyperchem. 7.51 version, computational studies *i.e.* 3D molecular modeling was done for compounds *i.e.* ligand as well as its metal(II) complexes. By using above computational tool, we were able to determine some significance parameters energy like bond angle, distance between two atoms *i.e.* bond length, energy levels and also some important parameters. For receiving better clarity hydrogen atoms were barred. To get the realistic molecular geometries of low energy, various modifications in the molecular coordinates were performed. Many cycles of energy minimization has to be done for each compound.

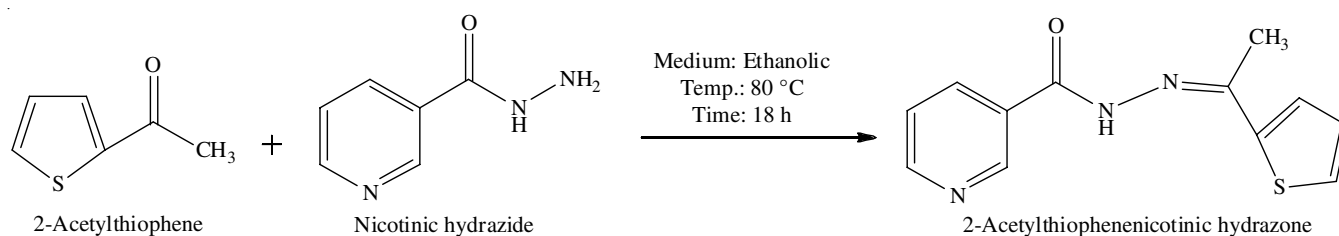
Antifungal activity: To analyze the antifungal activity of all the synthesized compound poisoned food method was followed to find out exact inhibition zone [36,37]. In this method, particular concentration of tested compound was prepared and

then incorporated into molten agar. Now this prepared content was transferred into disposable petri plates. Note these prepared plates were ready for incubation procedure. After pre-incubation, the inoculation can be done by used fungi *i.e.* *A. niger*, *M. phasolina* and *P. glomerata* ranging from 2-5 mm, which was deposited in the center of the plate. All tested plates as well as control and standard drug plates were incubated for about 24 h. Diameter of inhibition of tested compound has been compared with standard drug.

Antibacterial activity: The antibacterial activity was evaluated by using well diffusion method [38,39]. Bacteria *i.e.* *E. coli* and *P. aeruginosa* have been used for examine antibacterial property of newly synthesized compounds. As a roll part of media and standard drug, nutrient agar and neomycin have been used, respectively. After the preparation of aqueous solution of media, the prepared solution was autoclaved to kill the presence of any microorganism. The obtained content was then transferred into the petri plates in a UV chamber and allowed to cool first at room temperature and then in the refrigerator. Now again in UV chamber wells were prepared in media. Then by using sterilized swab stick microorganisms have been spread out on the surface of media and tested compound also poured into prepared wells. After completion of this procedure, tested plates were covered by lid and air tight by using Teflon tap. All the prepared plates were incubated for 24 h and then inhibition was measured.

Synthesis of 2-acetylthiophenenicotinic hydrazone: 2-Acetylthiophenenicotinic hydrazone (ATINH) as Schiff base ligand has been designed and synthesized by following condensation reaction. In this reaction, hot ethanolic solution of reactants *i.e.* 2-acetylthiophene (0.001 mol, 0.126 g) and nicotinic hydrazide (0.001 mol, 0.137 g) was refluxed on a hot plate and mixed well with attached magnetic stirrer on hot plate. Reaction content was refluxed for a time period 18 h at 80 °C. Now, the reaction solution was cooled at room temperature and then allowed to cool in an ice bath. After 1 h, white coloured solid was precipitated out and filtered by using vacuum, for washing double distilled water and cold ethanol used as solvent and washed product dried in a vacuum desiccator. Synthesis procedure for ATINH has been presented in **Scheme-I**.

Synthesis of Co(II) and Cu(II) complexes with synthesized bidentate ligand: All the cobalt and copper complexes of bidentate ligand were synthesized by the condensation reaction. Metal(II) complexes were obtained when ethanolic solution of Schiff base ligand (0.002 mol) was mixed and refluxed with ethanolic chloride as well as acetate salts of Co(II) and Cu(II) (0.001 mol) with constant stirring. After a particular time period for each complex content in a round bottom flask, was cooled



Scheme-I: Synthesis scheme for Schiff base ligand

firstly at room temperature and then on ice bath. After cooling, the coloured solid product was precipitated and filtered off. Then washed with cold ethanol and dried.

RESULTS AND DISCUSSION

Some analytical and physical parameters of ATINH and its cobalt and copper complexes are presented in Table-1. The ligand, 2-acetylthiopheneticotinichydrazone formed thermally stable metal complexes. All the complexes were characterized to investigate chemical structures and their composition by using various analytical and spectroscopic techniques. All the synthesized ligand as well as its metal(II) complexes were found non-hygroscopic in nature. On the basis of elemental analysis, it is concluded that metal complexes possesses the following composition *i.e.* $M(L)_2X_2$, where $M = Co(II)/Cu(II)$ ions, $L = ATINH$ bidentate ligand and $X = anions (Cl^-, CH_3COO^-)$, respectively. The molar conductance value ($\Omega^{-1} cm^{-1} mol^{-1}$) of complexes indicated that anions are present from outside from the coordination sphere, which shows non-conductive nature of complexes [40,41]. Ligand is soluble in ethanol while the metal(II) complexes are insoluble. All the synthesized metal complexes are soluble in dimethylsulphoide (DMSO) as well as in dimethylformamide (DMF).

IR studies: In the spectrum of ATINH, presence of specific IR bands at positions 1607 and 1699 cm^{-1} , correspond to the presence of imine group as well as oxygen atom of nicotinic hydrazone group, respectively (Fig. 1) [42,43]. In case of Co(II) and Cu(II) metal complexes, IR bands shifted downward which indicates that nitrogen atom of azomethine group (appeared at position 1587-1560 cm^{-1}) and oxygen atom of (C=O) group (appeared at position 1677-1658 cm^{-1}) coordinated to metal ion. Some characteristic bands are also appeared at 449-426 and 545-529 cm^{-1} , which support coordination of nitrogen as well as of oxygen donor atoms to metal ions, respectively [44, 45]. In case of chloride complexes, metal-chloride bonding is confirmed by appearance of peak at specific place *i.e.* 328 cm^{-1} [46]. Bonding of acetate ion to metal is supported by the appearance of IR bands at positions 1443-1441 and 1344-1277 cm^{-1} (Table-2). Monodentate coordination of acetate anion has been pointed out on the basis of appearance of these IR bands [47].

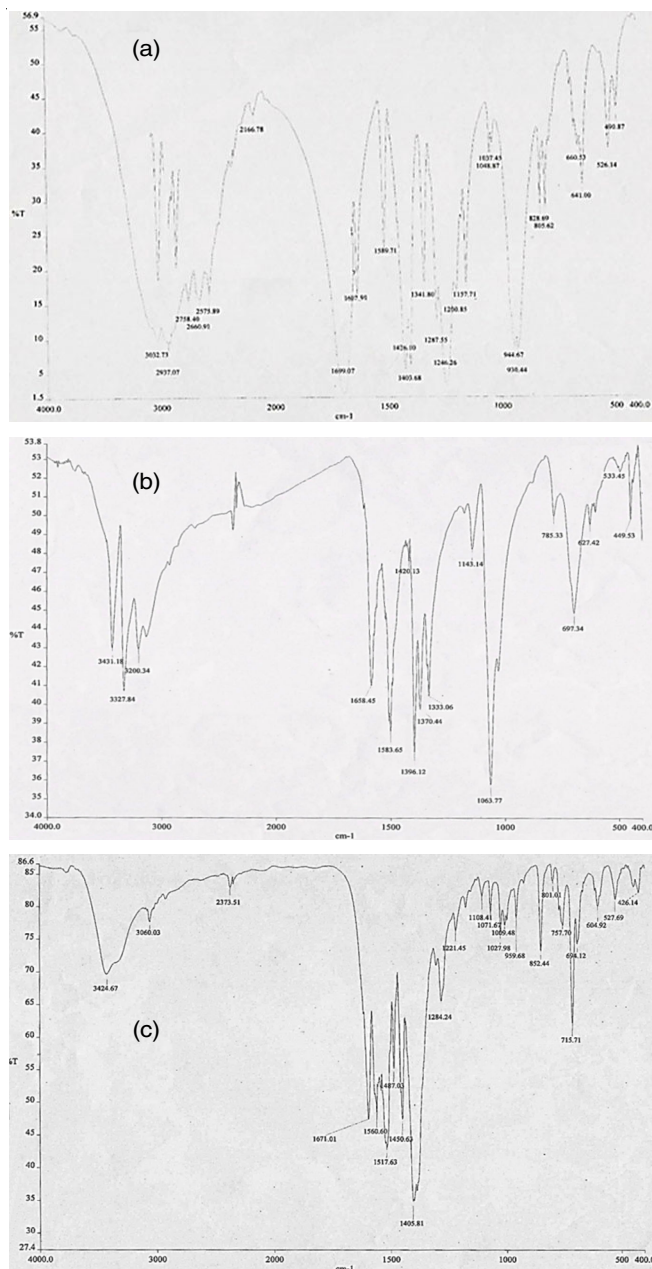


Fig. 1. IR spectra of (a) Schiff base (b) $[Co(L)_2Cl_2]$ complex (c) $[Cu(L)_2Cl_2]$ complex

TABLE-1
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF SCHIFF BASE AND ITS Co(II), Cu(II) COMPLEXES

Compounds	Molar ratio (M:L)	Colour	m.w. (g/mol)	m.p. ($^{\circ}C$)	Molar conductance ($\Omega^{-1} cm^2 mol^{-1}$)	Yield (%)	Time (h)	Elemental analysis (%): Calcd. (found)				
								C	H	N	Co(II)	Cu(II)
Ligand $C_{12}H_{11}N_3OS$	–	White	–	180	–	69	18	54.53 (54.69)	4.10 (4.17)	15.82 (15.95)	–	–
$[Co(L)_2Cl_2]$ $C_{18}H_{19}N_3O_5Co$	1:2	Light brown	652.47	>250	19	52	16	44.13 (44.06)	3.37 (3.34)	12.87 (12.81)	8.41 (8.36)	–
$[Co(L)_2(OAc)_2]$ $C_{17}H_{14}N_4O_6Co$	1:2	Brown	699.47	>260	25	60	18	48.03 (47.95)	4.00 (3.93)	12.00 (11.95)	7.85 (7.81)	–
$[Cu(L)_2Cl_2]$ $C_{24}H_{22}N_6O_2S_2CuCl_2$	1:2	Green	529.5	>250	19	52	16	50.85 (50.88)	3.58 (3.55)	9.12 (9.10)	–	10.35 (10.35)
$[Cu(L)_2(OAc)_2]$ $C_{28}H_{28}N_6O_6S_2Cu$	1:2	Green	542.5	>260	25	60	18	22.66 (22.65)	1.25 (1.25)	17.62 (17.60)	–	13.58 (13.60)

TABLE-2
CHARACTERISTIC INFRARED SPECTRAL BANDS FOR LIGAND AND ITS Co(II) AND Cu(II) COMPLEXES

Compounds	Spectral bands (cm ⁻¹)				Bands due to anions
	v(C=N)	v(C=O)	v(M-N)	v(M-O)	
Ligand	1607	1699	–	–	–
[Co(L) ₂ Cl ₂]	1583	1658	449	533	Band at 328 cm ⁻¹ recommend the presence of Co-Cl bond
[Co(L) ₂ (OAc) ₂]	1587	1664	426	529	v _{as} (OAc) = 1441, v _s (OAc) = 1344, Δv = 97 cm ⁻¹ recommend monodentate nature of acetato group
[Cu(L) ₂ Cl ₂]	1560	1671	426	527	Band at 328 cm ⁻¹ recommend the presence of Cu-Cl bond
[Cu(L) ₂ (OAc) ₂]	1575	1677	432	545	v _{as} (OAc) = 1443, v _s (OAc) = 1277, Δv = 166 cm ⁻¹ recommend monodentate nature of acetato group

Magnetic moment: The experimentally value for magnetic moment of cobalt and copper complexes lies in the range of 4.73-4.82 B.M. and 1.92-2.01 B.M, respectively (Table-3). These values indicate the presence of three and one unpaired electron cobalt and copper complexes. These values are in support of paramagnetic nature as these values are very well closed and agreed with the theoretically calculated value of synthesized metal complexes [48,49].

TABLE-3
ELECTRONIC SPECTRAL BANDS AND MAGNETIC MOMENT OF SYNTHESIZED METAL COMPLEXES

Complexes	Electronic spectral bands (cm ⁻¹)				μ _{eff} (B.M.)
	v ₁	v ₂	v ₃	v ₄	
[Co(L) ₂ Cl ₂]	9766	17002	25315	36783	4.73
[Co(L) ₂ (OAc) ₂]	9916	18622	30003	35587	4.79
[Cu(L) ₂ Cl ₂]	10173	18975	26274	37847	1.96
[Cu(L) ₂ (OAc) ₂]	10695	19066	27919	38023	1.98

Electronic spectra: The UV-visible spectra of Co(II) complexes was taken in DMSO (Fig. 2). In Table-3, UV-visible spectral data is summarized. For cobalt *d*⁷, F term has been used as ground state of free ion, whose degeneracy is lifted by an octahedral field to give a ⁴T_{1g} ground state. The determinant as given in following equation suffice to determine the energies of ⁴T_{1g} (F) and ⁴T_{1g} (P) levels. The determination in the above equation gives the energies of the T₁ levels relative to the atom in the ground state in the spherical field rather than to give the transition energies but the difference between the root, namely (225B² + 100 Dq² - 180B Dq²)^{1/2} is the transition energy ⁴T₁(F) → ⁴T_{1g} (P). Following bands are observed for cobalt metal complexes *i.e.* 9569-9921 cm⁻¹, 17002-20560 cm⁻¹ and 20763-32051 cm⁻¹ and these transitions may be assigned as ⁴T_{1g} → ⁴T_{2g}(v₁), ⁴T_{1g} → ⁴T_{1g}(F), ⁴T_{1g}(F) → ⁴A_{2g}(v₂), ⁴T_{1g}(F) → ⁴T_{1g}(P) (v₃) transitions, respectively. On the basis of these transition states, six coordinated octahedral geometry has been assigned for the complexes [50,51]. The absorption bands of UV-visible spectra of copper complexes appeared in the range of 9766-11211, 17002-19066 and 25315-30003 cm⁻¹. These following *d-d* transition s have been assigned for the observed absorption bands following *i.e.* ²A_{1g} → ²B_{1g} (v₁), ²B_{2g} → ²B_{1g} (v₂) and ²E_g → ²B_{1g} (v₃). High energy absorption band present in the range of 35587-39646 cm⁻¹ correspond to the ligand metal charge. On the basis of UV visible spectra data, copper complexes possessed six coordinated distorted octahedral geometry [52].

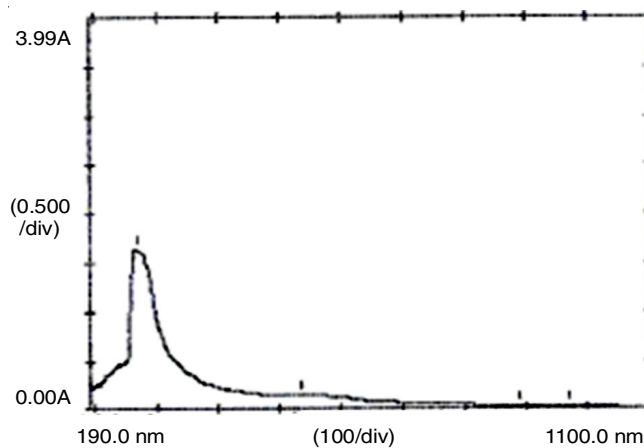


Fig. 2. Electronic spectrum of [Co(L)₂(OAc)₂] complex

Ligand field parameter: On the basis of absorption bands some significant ligand field parameters for cobalt complexes have been calculated and presented in Table-4. Dq LFP is an important parameter, which has been calculated by using first absorption band *i.e.* v₁ [53]. By using the following relation β = B_(complex)/B_(free ion), parameter which is known as nephelauxetic has been calculated (value of B_(free ion) for Co(II) metal is 1120 cm⁻¹). If value of β is found less than one it shows covalent character between metal ligand (ML) bond. In case of cobalt complexes of ATINH, value of β is in range of 0.54-0.88 cm⁻¹. These values are in strong support that covalent character is present in ML bond [54].

TABLE-4
CALCULATED LIGAND FIELD PARAMETERS FOR Co(II) COMPLEXES

Complexes	Dq (cm ⁻¹)	B (cm ⁻¹)	β	LFSE (Kjmol ⁻¹)
[Co(L) ₂ Cl ₂]	976	867	0.77	140.18
[Co(L) ₂ (OAc) ₂]	991	852	0.83	142.33

Electronic paramagnetic resonance (EPR) studies: The electronic spectra of spectra of cobalt and copper complexes of ATINH ligand have been taken in the form of polycrystalline state at temperature 300 K under a magnetic field whose strength is 3000 G at the frequency of 9.1 GHz. Theory of octahedral case of cobalt and copper metal ion (in complex form) *i.e.* *d*⁷ and *d*⁹ system has been recognized by slightly distortion which is based on John-teller concept and geometry with this distortion known as distorted octahedral or tetragonal. They found

that the value g for transition between the two states of Kramer's doublet was very sensitive to distortion in crystal field and were able to account for observed values readily in term of the theory. The values of g_{\parallel} , g_{\perp} and g_{iso} were found to be 2.32-2.54, 2.04-2.15 and 2.22-3.6, respectively (Table-5). The values of g_{\parallel} and g_{\perp} have been found less than 2.58, which are in high support of distorted geometry *i.e.* tetragonal geometry [55].

TABLE-5
EPR DATA OF Co(II) AND Cu(II) COMPLEXES

Complexes	g_{\parallel}	g_{\perp}	g_{iso}
[Co(L) ₂ Cl ₂]	2.54	2.14	2.27
[Co(L) ₂ (OAc) ₂]	2.38	2.15	2.22
[Cu(L) ₂ Cl ₂]	2.32	2.04	3.6
[Cu(L) ₂ (OAc) ₂]	2.45	2.05	3.3

Computation study: Several attempts have been made for growing single crystal of ATINH ligand as well as of metal complexes but no crystal grown. So to find out structural information of ligand and metal complexes, computational studies *i.e.* molecular modeling has been done by using 7.51 version in the gas phase of Hyperchem software. Basically computational study gives some specific information of compounds *i.e.* structural information, some parameters like bond length, bond angle, bond energy, *etc.* Not only spectral studies but also molecular modeling studies revealed six coordinated geometry for all the metal(II) complexes. Optimized structure of ATINH ligand and its complexes have been presented in Fig. 3 and the specific data are represented in Table 6 and 7.

In vitro Antimicrobial activity: Mononuclear complexes of novel ATINH ligand have been screened to investigate the *in vitro* antimicrobial activity against the growth of studied

TABLE-6
OPTIMIZED GEOMETRY OF THE SCHIFF BASE AND ITS METAL COMPLEXES (BOND LENGTHS IN ANGSTROMS)

Atom-atom-atom for Co(II) complexes	[Co(L) ₂ Cl ₂]	[Cu(L) ₂ Cl ₂]	Atom-atom-atom for Cu(II) complexes	[Co(L) ₂ (OAc) ₂]	[Cu(L) ₂ (OAc) ₂]
2-1-5	91.0868	79.8545	2-1-5	90.4007	80.4996
5-1-19	90.3128	91.9828	5-1-19	95.1699	102.52
19-1-28	92.4524	95.0688	19-1-28	90.4886	91.0083
28-1-36	86.0847	87.937	28-1-36	88.6411	90.2788
36-1-37	87.4813	85.2514	36-1-5	171.611	156.544
37-1-2	85.4928	82.1122	36-1-19	93.1959	99.3701
37-1-19	169.867	171.41	36-1-2	81.222	76.7154
36-1-5	174.05	156.104	2-3-4	119.489	114.603
36-1-19	89.6203	89.2312	19-1-28	90.4886	91.0083
37-1-5	91.5674	90.419	28-29-30	120.102	122.338
37-1-28	97.0312	91.3135	5-6-7	124.59	125.163
36-1-2	82.9845	76.2767	19-20-21	119.295	122.837
2-3-4	118.947	113.007	2-3-13	121.886	127.251
19-1-28	92.4524	95.0688	8-9-10	91.1423	91.0837
28-29-30	121.225	122.138	31-33-35	91.6427	91.9786
5-6-7	126.993	123.869	36-1-40	88.4778	90.3619
19-20-21	120.595	119.367	40-41-42	124.849	106.48
2-3-13	119.928	129.252	40-41-43	112.007	128.532
8-9-10	92.0196	91.3284	36-37-39	122.738	111.476
31-33-35	92.3068	91.8214	36-37-38	113.564	125.14
			38-37-39	123.287	123.366
			40-1-19	82.527	90.037
			40-1-28	172.283	178.114
			40-1-2	90.0114	82.4
			40-1-5	91.9888	81.1208

TABLE-7
OPTIMIZED GEOMETRY, VARIOUS ENERGIES AND HEAT OF FORMATION OF Co(II) AND Cu(II) COMPLEXES

	[Co(L) ₂ Cl ₂]	[Cu(L) ₂ Cl ₂]	[Co(L) ₂ (OAc) ₂]	[Cu(L) ₂ (OAc) ₂]
Geometry optimization	Semiempirical, PM3	Semiempirical, PM3	Semiempirical, PM3	Semiempirical, PM3
Geometry	Octahedral	Computed	Octahedral	Computed
Convergence limit	0.0100000	0.0100000	0.0100000	0.0100000
Iteration limit	50	50	50	50
Accelerate convergence	YES	YES	YES	YES
Total energy (kcal/mol)	-150833.1605511	-159777.9940996	-176387.9838852	-185367.3883814
Binding energy (kcal/mol)	-6554.5968831	-6223.6044016	-7591.2001874	-7591.2001874
Isolated atomic energy (kcal/mol)	-144278.5636680	-153554.3896980	-176387.9838852	-177776.1881940
Electronic energy (kcal/mol)	-1463993.4794310	-1486885.1283529	-1944897.1533900	-1968820.7370932
Core-core interaction (kcal/mol)	1313160.3188799	1327107.1342533	1768509.1695047	1783453.3487118
Heat of formation	-216.6948831	92.5975984	-373.2917212	-98.5701874

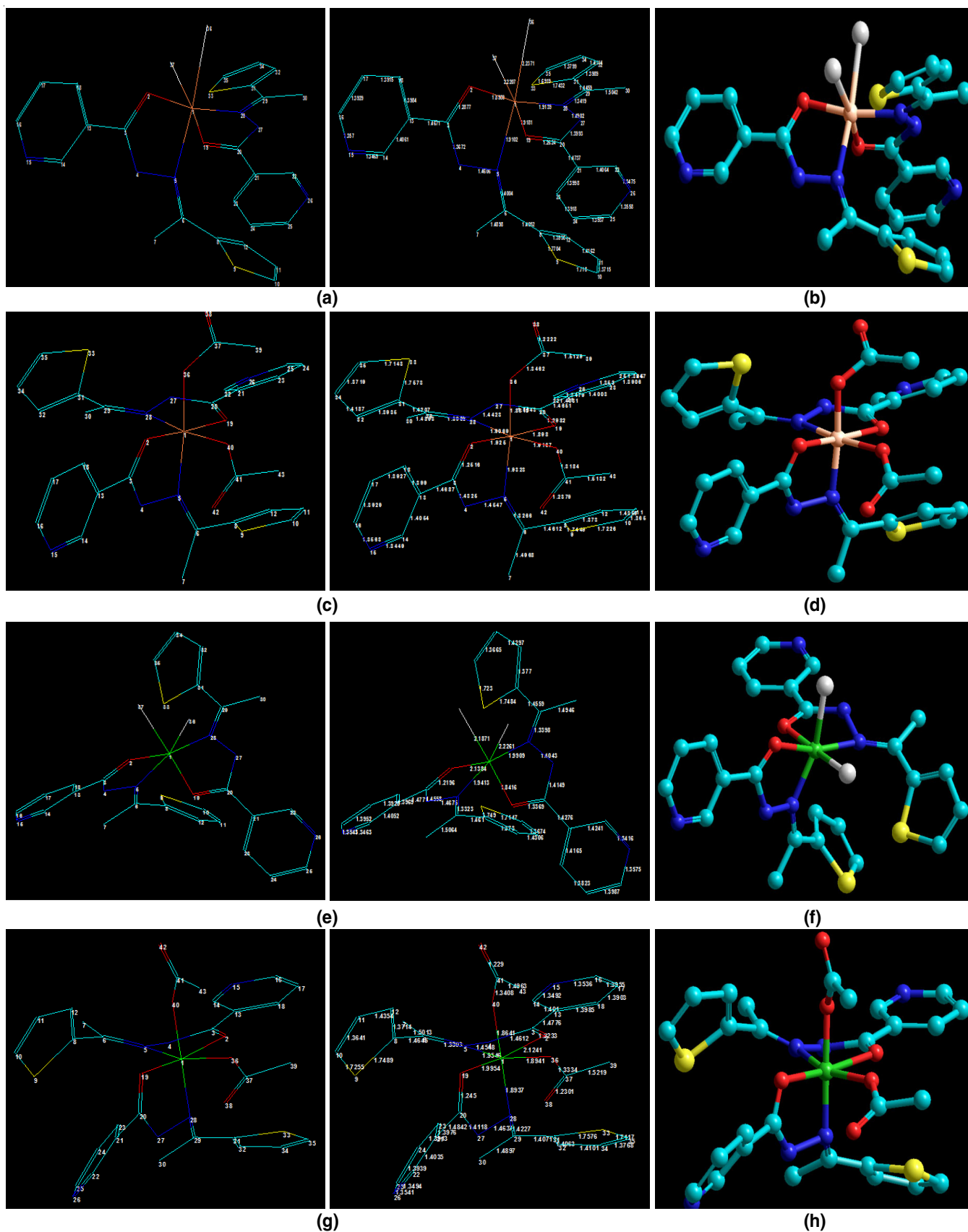
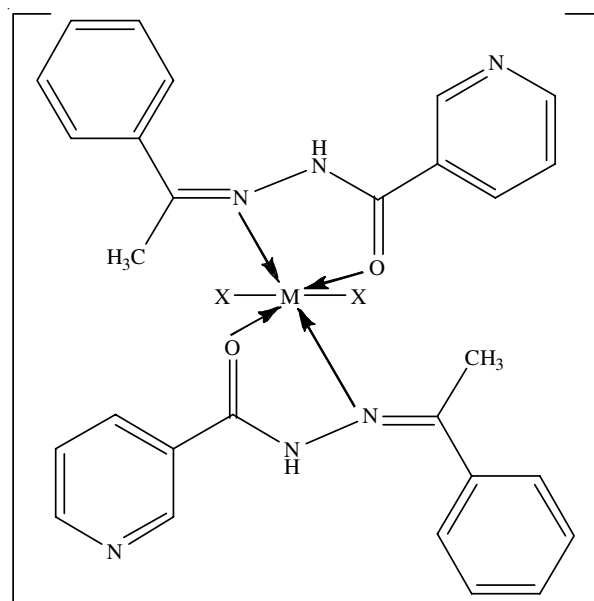


Fig. 3. Optimized geometry of Co(II) complexes (a) representation of bond angles of $[\text{Co}(\text{L})_2\text{Cl}_2]$ complex, (b) ball and stick model presentation of $[\text{Co}(\text{L})_2(\text{OAc})_2]$, (c) representation of bond angles of $[\text{Co}(\text{L})_2\text{Cl}_2]$ complex, (d) ball and stick model presentation of $[\text{Co}(\text{L})_2(\text{OAc})_2]$, (e) representation of bond angles of $[\text{Cu}(\text{L})_2\text{Cl}_2]$ complex, (f) ball and stick model presentation of $[\text{Cu}(\text{L})_2\text{Cl}_2]$, (g) representation of bond angles of $[\text{Cu}(\text{L})_2(\text{OAc})_2]$ complex, (h) ball and stick model presentation of $[\text{Cu}(\text{L})_2(\text{OAc})_2]$

fungi *A. niger*, *M. phaseolina* and *P. glomerata* and bacteria *E. coli* and *P. aeruginosa*. The tested compounds were compared with standard fungicide and bactericide drugs chlorothalonil and neomycin, respectively. Screening data of both activities of ligand as well as its metal(II) complexes is accessible in Table-8. At the concentration 1000 ppm $[\text{Cu}(\text{ATINH})_2\text{Cl}_2]$ complex exhibited higher activity compared to other synthesized compounds. Moreover, it was found that $[\text{Co}(\text{ATINH})_2\text{Cl}_2]$ complex is more active against *P. aeruginosa*, while $[\text{Co}(\text{ATINH})_2(\text{OAc})_2]$ and $[\text{Cu}(\text{ATINH})_2(\text{OAc})_2]$ complexes show significance inhibition zone for *E. coli*. Thus, it is concluded that metal(II) complexes exhibited more inhibition against growth of taken microorganism [56,57].

Conclusion

This research work includes the investigation and interaction between newly synthesized bidentate Schiff base ligand *i.e.* 2-acetylthiophenenicotinic hydrazone (ATINH) and different anions (Cl^- and CH_3COO^-) of cobalt(II) and copper(II) ions. Using analytical and spectral studies, it is demonstrated that ATINH coordinate to cobalt(II) and copper(II) ions with its potential donor atoms *i.e.* nitrogen and oxygen and two counter ions. Physical and spectroscopic characterization data suggested that metal complexes are neutral, mononuclear and possess octahedral geometry Fig. 4, which is further supported by computational study. ATINH and its complexes $[\text{Co}(\text{ATINH})_2\text{Cl}_2]$, $[\text{Cu}(\text{ATINH})_2\text{Cl}_2]$, $[\text{Co}(\text{ATINH})_2(\text{OAc})_2]$, $[\text{Cu}(\text{ATINH})_2(\text{OAc})_2]$



where, M = Co(II), Cu(II); X = Cl^- , CH_3COO^-

Fig. 4. Proposed structure of mononuclear complexes of ligand 2-acetylthiophenenicotinic hydrazone

have been investigated for their *in vitro* antimicrobial activity. It is concluded that cobalt(II) and copper(II) complexes have been found more active than ligand. The $[\text{Cu}(\text{ATINH})_2\text{Cl}_2]$ complex acts as a good antifungal agent while $[\text{Co}(\text{ATINH})_2$

TABLE-8
ANTIFUNGAL AND ANTIBACTERIAL ACTIVITIES DATA OF SYNTHESIZED LIGAND AND ITS Co(II) AND Cu(II) COMPLEXES

Compounds	Concentration (ppm)	Inhibition (%)				
		Antifungal activity			Antibacterial activity	
		<i>A. niger</i>	<i>M. phaseolina</i>	<i>P. glomerata</i>	<i>E. coli</i>	<i>P. aeruginosa</i>
Ligand (L)	1000	30	30	25	10	No activity
	750	25	15	20		
	500	20	10	15	05	No activity
	250	No activity	No activity	No activity		
$[\text{Co}(\text{L})_2\text{Cl}_2]$	1000	50	30	35	25	30
	750	35	20	25		
	500	20	NA	15	10	20
	250	10	NA	10		
$[\text{Co}(\text{L})_2(\text{OAc})_2]$	1000	20	40	50	30	25
	750	10	35	40		
	500	No activity	20	25	20	15
	250	No activity	10	15		
$[\text{Cu}(\text{L})_2\text{Cl}_2]$	1000	95	90	95	25	05
	750	80	80	55		
	500	60	45	35	10	No activity
	250	45	30	10		
$[\text{Cu}(\text{L})_2(\text{OAc})_2]$	1000	90	85	60	30	20
	750	75	60	55		
	500	60	55	30	25	05
	250	45	35	25		
Chlorothalonil	1000	100	100	100		
	750	95	95	95		
	500	90	90	85		
	250	85	75	80		
Neomycin	1000				45	30
	500				42	25

Cl₂], [Co(ATINH)₂(OAc)₂] and [Cu(ATINH)₂(OAc)₂] show the higher inhibition and act as good antibacterial agent against growth of bacteria. Antimicrobial study also showed that all examined compounds exhibit less activity than used standard fungicide and bactericide drugs chlorothalonil and neomycin, respectively.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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