Synthesis, Characterization and Bioactivity of Cobalt(II) Complexes with Benzoylidenepyridine-2-, 3- and 4-hydroxyaniline and Nitrate or Perchlorate as Coligands

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Novel metal complexes of cobalt(II) with benzoylidenepyridinebenzoylidenepyridine-3-hydroxy-2-hydroxyaniline (BP2HA), aniline (BP3HA), benzoylidenepyridine-4-hydroxyaniline(BP4HA) and nitrate or perchlorate as coligands have been synthesized and characterized by elemental analyses, molar conductance, magnetic susceptibility, electronic, vibrational, NMR, EPR and thermal studies. The molar conductance data revealed that complexes with nitrate as coligand are neutral and the complexes with perchlorate as coligand are ionic. The crystal field splitting parameters (Dq, B', \beta, LFSE and CFSE) have been calculated from the electronic spectral data for the proposed octahedral geometry. IR spectral data revealed the involvement of azomethine nitrogen and pyridine nitrogen in coordination with the metal ion. The magnetic moment and EPR data suggested the presence of high spin cobalt(II) in the complexes. The thermogravimetric analysis showed that the complexes are stable up to 125°C. The complexes, free ligands and their corresponding metal salts have been screened for antimicrobial activity. Complexes are found to be highly active compared to the corresponding ligands and metal salts. Among the test microbes, Staphvlococcus aureus showed no effect against metal complexes whereas Escherichia coli and Streptococus albicans were more sensitive to all the test chemicals.

Key Words: Benzoylidenepyridine (-2-, 3- and 4-hydroxy aniline, Cobalt(II) complexes, Bioactivity.

INTRODUCTION

The design and complex chemistry of novel nitrogen-donor multidentate ligands and the study of their physical properties are of interest due to their potential applications in areas such as catalysis¹, magnetism, sensors and modeling of biological importance^{2,3}. Considerable interest has been shown in metal complexes of Schifff base derivatives of pyridines^{4,5} especially those having NN and NNS donor sequences. These compounds warrant further study because they provide an interesting series of complexes by the isomeric ligands. The synthesis and spectroscopic characterization of [Co(III) (salophen)(amine)₂]ClO₄ com-

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plexes where salophen = N,N'-salicylidene-1,2-phenylenediamine dianion and amine = morpholine⁶, pyrrolidene⁷ and piperidine⁸ have been reported. The crystal structure of [Co(III)(salophen)(morpholine)₂]ClO₄ and [Co(III)(salophen)-(pyrrolidene)₂]ClO₄ have also been reported⁹. Synthesis and antimicrobial activity of copper(II), cobalt(II) and nickel(II) complexes with Schiff bases, 3-(4'-phenylthiazole-2'-yl)-1-(2'-hydroxy-1-aminophenyl)urea and with 3-(4'-phenylthiazole-2'-yl)-1-(2',4'-dihydroxy/2'-hydroxy-5'-chloro-1'-methylimino-methylphenyl)urea have also been reported¹⁰ in which metal ion exhibits coordination number six, oxidation state two and octahedral geometry. We report herein the synthesis, characterization and bioactivity of some cobalt(II) complexes of Schiff bases (Fig. 1) formed between benzoylpyridine and 2-, 3- or 4-hydroxyaniline.

Fig. 1. Structure of the ligand

EXPERIMENTAL

Preparation of ligands and complexes

Synthesis of benzoylidenepyridine-n-hydroxyaniline (BPnHA): All the reagents used were of AR grade. Benzoylation was carried out by the modified Jensen method in which ethanol was used as a solvent instead of benzene and ice cooled 5 N HCl acid was used for neutralization to give better yield¹¹. Pyridine was converted to benzoyl pyridine by refluxing pyridine (142 mmol) in ethanol, calcium hydroxide (100 mmol) and benzoylchloride (142 mmol) for 2–3 h and on cooling followed by neutralization. White shining crystals of benzoylchloride were obtained by recrystallization from hot ethanol. The TLC analysis of benzoylchloride gave a single spot indicating the presence of only one isomer. The melting point of the benzoylpyridine was found to be 46°C which corresponds to the melting point of 2-benzoylpyridine (m.p. of 2-benzoylpyridine is 42-44°C, of 3-benzoylpyridine is 117–119°C and of 4-benzoylpyridine is 70–75°C). Schiff bases were prepared by the refluxing equimolar solution of 2-, 3-or 4-aminophenol with benzoyl pyridine for 4–6 h in ethanol. Brown crystals of Schiff bases were obtained.

Synthesis of complexes: The complexes (I, II, III) were prepared by the condensation of Schiff bases (20 mmol) and cobalt(II) nitrate (10 mmol) (2:1) in ethanol and refluxing for 4–6 h. The light brown solution turned deep brown immediately upon the complex formation. The solvent was evaporated and the crude products were washed with petroleum ether 10–15 times to remove the unreacted ligands and metals. The crystalline precipitates were dried over CaCl₂

(yield ca. 80%). In a similar way, the complexes (IV, V and VI) were prepared by the condensation of cobalt perchlorate and Schiff bases in 1:3 stoichiometric ratio in ethanol. Cobalt(II) perchlorate salt was prepared by treating CoCl₂ with NaClO₄. [Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive and limited analyses were carried out for perchorate complexes.]

Melting points were taken in open capillaries and were unconnected. CHN analyses were performed by using a Perkin-Elmer 112400 CHN rapid elemental analyzer. The metal contents were estimated as the metal oxides¹², Molar conductance of the complexes was determined in 10⁻³ M DMF solutions using a Dalal model 602 M conductivity meter using a dip cell and 0.1 N KCl as the calibrant at room temperature. The magnetic susceptibility was determined by VSM technique at room temperature and it was calculated by considering the diamagnetic corrections 13. The vibrational spectra were recorded on Perkin-Elmer 598 spectrophotometer in the region of 4000-400 cm⁻¹. Electronic spectra were recorded on a Hitachi-380 spectrophotometer. EPR spectra were recorded on Bruker IPS spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker AMX-400 (400 mHz) in CDCl₃. Thermal analyses were carried out on Seiko-TGA instrument with a linear heating rate of 10°C/min in an inert helium atmosphere.

Biological activity

Test microorganisms: Six microbes were used to test the biological potential of the metal salts, ligands and their complexes. They were Escherichia coli (G, causes dysentery), Staphylococcus aureus (G, causes throat infection), Klebsiella pneumoniae (G-, causes pneumonia), Candida albicans (causes scabies), Streptococus albicans (G+, abscess formation) and Pseudomonas aeruginosa (G²⁻, converts insoluble phosphate to phosphorus).

Antimicrobial activity

Antimicrobial activity of each sample was qualitatively determined by disc diffusion method^{14, 15}. Antimicrobial activity was indicated by the presence of clear inhibition zone around the discs on a Mueller-Hinton agar medium (medium is the composition of casein acid hydrolysate, beef extract, starch and agar).

Microbes which showed maximum (10 mm) inhibition zone by disc diffusion technique were selected and were subjected to the serial dilution method of microbiostatic(inhibitory) activity 16. The lowest concentration that completely inhibited visible microbial growth was recorded as the minimum inhibitory concentration (MIC, µg/mL). For MIC, all the test chemicals were prepared in series of concentration and mixed with sterile Leuria Bertanii (LB) broth. Selected microbes for MIC were inoculated and incubated in the incubator. Growth of microbe was indicated by turbidity formation. The specific concentration of the test samples inhibiting the growth of the microbes was noted¹⁷.

RESULTS AND DISCUSSION

The elemental analysis, molar conductance and magnetic moment values are given in Table-1 which confirm that the complexes (I, II and III) are neutral and complexes (IV, V and VI) are ionic

TABLE-I ANALYTICAL DATA OF Co(II) COMPLEXES

Complexes	No. Colo		m.p.	g	Found (calcd.) (%)				A **	µeff (B.M.)
·		. colour	(°C)	g	С	Н	N	Co	-/ N _{PM} '	Expt. (Calcd.)
[Co(BP2HA) ₂ (NO ₃) ₂]	I	Dark brown	170	2.0006	58.98 (59.10)	3.74 (3.80)	11.47 (11.40)	7.55 (8.00)	50	3.52 (3.87)
$[Co(BP3HA)_2(NO_3)_2]$	II	Brown	151	2.0006	58.71 (59.10)	3.89 (3.80)	11.36 (11.40)	8.21 (8.00)	45	3.51 (3.87)
$[Co(BP4HA)_2(NO_3)_2]$	III	Dark brown	185	2.0006	59.01 (59.10)	3.43 (3.80)	11.21 (11.40)	7.32 (8.00)	55	3.52 (3.87)
[Co(BP2HA) ₃ (ClO ₄) ₂]	IV	Dark brown	179	niterature.	58.98 (59.10)	3.81 (3.80)	11.53	-Problem	180	3.43 (3.87)
[Co(BP3HA) ₃ (ClO ₄) ₂]	V	Dark brown	190	-	58.79 (59.10)	3.74 (3.80)	11.31 (11.40)		190	3.51 (3.87)
[Co(BP4HA) ₃ (ClO ₄) ₂]]	VI	Dark brown	187		59.18 (59.10)	3.71 (3.80)	11.22 (11.40)		170	3.46 (3.87)

^{*}Molar conductance (ohm⁻¹ cm mol⁻¹)

Complexes (I, II and III) were insoluble in water and the common organic solvents like ethanol, benzene, water, chloroform, but they were soluble in acetone, DMF, DMSO and nitrobenzene. Complexes (IV, V and VI) are soluble in water and in organic solvents like chloroform, ethanol, acetone, DMF, DMSO and nitrobenzene. The molar conductance of (10⁻³ M solution) in DMF of complexes (I, II and III) (45–55 ohm⁻¹ cm² mol⁻¹) indicated the non-electrolytic nature and the complexes (IV, V and VI) (170–190 ohm⁻¹ cm² mol⁻¹) indicated the ionic (1:2 electrolytic) behaviour of the perchlorate complexes ¹⁸. The magnetic moment values of these complexes are within the range of 3.87–4.00 B.M. which favoured the presence of cobalt in the +2 oxidation state and leaving the complexes as high spin complexes with the configuration $t_g^5 e_g^2$.

The electronic spectra of the complexes dissolved in DMF show the modification of the absorption bands (Table-2). The electronic spectra of the ligands (VII, VIII and IX) consist of a relatively intense band centred at 284, 280 and 263 nm respectively. These were assigned to $\pi \to \pi^*$ transition and a second band respectively at 391, 383 and 380 nm corresponds to $n \to \pi^*$ excitation. After complexation with cobalt(II), several transitions appear below 362 nm still involving principally interligand $\pi \to \pi^*$ transitions. The electronic spectra of the complexes (I, II and III) have absorbtion maxima (nm) respectively at 490 (20,408), 432 (23,148), 363 (27,548), 263 (38,028), 560 (17,857), 400 (25,000), 386 (25,906), 275 (36,363), 560 (17,857), 400 (25,000), 383 (26,109), 316

TABLE-2 ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF THE LIGANDS AND COBALT(II) COMPLEXES

Ligands	No	λ _{max} Tran (nm)	sition Complex	(nmi)	Transition	Δ_0 (cm ⁻¹)	B (cm ⁻¹)	β	CFSE (cm ⁻¹)	LFSE (kJ mol ⁻¹)
ВР2НА	VII	391 n— 284 π—	. 1	432	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$	13185	637	0.67	31052	126.2
ВРЗНА	VIII	383 n— 280 π—	- 1	400	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$	11770	535	0.55	32184	112.6
ВР4НА	IX	380 n→ 263 π→	- 1	400	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$	11770	535	0.55	32184	112.6
			IV	482	$^{4}T_{1g}(F) \rightarrow ^{4}T_{1g}(P)$ $^{4}T_{1g}(F) \rightarrow ^{4}A_{2g}(F)$	10890	495	0.51	32888	112.6
				520 482	$^{4}T_{1g}(F) \rightarrow ^{4}T_{1g}(P)$ $^{4}T_{1g}(F) \rightarrow ^{4}A_{2g}(F)$	10890	524	0.54	32936	103.6
			VI	482	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$	10830	524	0.54	32936	103.6

(31,645) (cm⁻¹). The electronic spectra of I-III having absorption maxima around 560 nm (490–560) were assigned to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and those of 263, 275 and 316 nm respectively for I, II and III were attributed to charge transfer transition $(n_{\pi} \rightarrow d_{\pi})$. The bands observed at 432 and 363, 400 and 386, 400 and 383 nm are attributed to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions due to high spin octahedral cobalt(II) $(t_{2g}^5 e_g^2)$. The Racah parameter B and covalency factor β were calculated using the ratios of the intensity of these transitions with reference to Tanabe-Sugano diagram $^{19-21}$ of high spin octahedral $3d^7$ system. The B value of the complexes (I, II and III) were found to be 0.67, 0.55 and 0.55 respectively. The Δ_0 values of complexes (I, II and III) were found to be 13185, 11770 and 11770 cm⁻¹ and the CFSE were calculated using $(-0.8 + 2P)\Delta_0$ and were found to be 31052, 32184 and 32184 cm⁻¹ respectively. The LFSE values were calculated using $(2/5p - 3/5q)\Delta_0$ and were found to be 126.2, 112.6 and 112.6 kJ mol⁻¹. Since $\Delta_0 < P$ (free cobalt ion (Co²⁺) ca. 20,800 cm⁻¹) the high spin state of cobalt(II) is proposed. The Δ_0 , CFSE and LFSE for the complexes (IV, V and VI) were calculated and are given in Table-2. The absorption bands in the region

500–560 nm, the values of the calculated ligand field parameters and the absence of perchlorate ion inside the coordination sphere indicate an octahedral geometry for the [Co(BPHA)₃](ClO₄)₂ complexes.

The ligands have three potential donor sites, heterocyclic (pyridine) nitrogen, phenolic —OH group and azomethine nitrogen. A comparative study of the IR spectra of the free ligands and the complexes (Table-3) evinces modifications of the vibration bands characteristic of the azomethinic group, v(C=N) and the skeletal vibration of the pyridine ring

TABLE-3
IR SPECTRAL DATA (cm⁻¹) OF LIGANDS AND COMPLEXES

VII	I	VIII	11	IX	III	Tentative assignment
3375	3400	3183	3398	3272	3392	Phenolic O—H
1220	1220	1229	1241	1220	1223	Phenolic v(C—OH)
1687	1635	1597	1504	1672	1608	v(C=N)
1602	1610	1672	1604	1572	1505	v(pyridine ring)
	1420		1491		1452	V ₄ (NO ₃)
	1384		1383		1383	$V_3(NO_3)$
	1112		1150		1132	$V_3(ClO_4)$
	1035		1120		1107	$V_2(NO_3)$
	628		552		510	(Co-N) (azomethine
	580		482		476	(Co—N) (pyridine)

The ligands are found to act as a bidentate ligand in which azomethine nitrogen and pyridine nitrogen can form bond with metal leaving the phenolic —OH as free —OH. The phenolic stretching vibration of v(O-H) is observed for the ligand VII at 3375 cm⁻¹ (broad) and is shifted to 3400 cm⁻¹ in the complex which is due to the breaking of the intramolecular hydrogen bond between phenolic hydrogen and azomethine nitrogen. In the case of the ligands VIII and IX, the same effect is observed due to the breaking of intermolecular hydrogen bonding. The appearance of $v(C\rightarrow O)$ (phenolic) at 1220 cm⁻¹ in the spectrum of the ligand and in those of the complexes I, II and III respectively at 1220, 1229 and 1220 cm⁻¹, indicates the non-involvement of the phenolic —OH group in coordination with the metal ion.

The sharp bands observed in VII, VIII and IX at 1687, 1672 and 1672 cm⁻¹ are shifted to lower frequencies in complexes I, II and III respectively at 1635, 1604 and 1608 cm⁻¹ indicating coordination of azomethine nitrogen to the central metal atoms. A medium intensity band assigned as the breathing mode of -C=N-C= of pyridine⁴ in VII, VIII and IX at 1602, 1672 and 1572 cm⁻¹ are shifted to 1610, 1604 and 1505 cm⁻¹ respectively in the complexes of I, II and III, which indicate the involvement of pyridine nitrogen in coordination with the metal atom. The IR spectrum of the complex exhibits three additional bands which have no parallel bands in the spectrum of the ligand. Three bands in I, II and III respectively at 1420, 1384, 1035 cm⁻¹, 1491, 1383, 1150 cm⁻¹ and 1383, 1132, 1107 cm⁻¹ are assigned respectively to v_4 , v_1 and v_2 modes of the coordination of the nitrate ion. The splitting determines the nature of coordination of the nitrate ion²² and (v_4-v_1) of I, II and III are respectively 36, 108 and 69 cm⁻¹ which indicates that nitrate ion

acts as a monodentate ligand. In the complexes of IV, V and VI, the sharp bands respectively at 1112, 1120 and 1132 cm⁻¹ are assigned to v₃ mode of uncoordinated perchlorate ion. The spectra of the complexes of I, II and III have two more additional bands respectively at 628, 580 cm⁻¹, 552, 482 cm⁻¹ and 510, 476 cm⁻¹ due to $v(M \rightarrow N_{azomethine})$ and $v(M \rightarrow N_{pyridine})$. Tentative structures of these complexes are shown in Fig. 2 and Fig. 3.

Fig. 2. Structure of nitrate complexes

Fig. 3. Structure of perchlorate complexes

The ¹H and ¹³C NMR spectra of BPHA in CDCl₃ showed resonance signals at 8.05, 7.5, 7.49, 7.41, 7.39, 7.35 δ and at 2.97 and 2.59 δ and in the complex at 8.02, 8.0, 7.98, 7.47, 7.45, 7.4, 7.38, 7.16, 6.47, 3.5, 2.56 and 1.82 δ. The intensity ratios obtained for these absorptions correspond to the total number of protons for each proton type. Offset scanning beyond $10\,\delta$ does not register any signal. The ¹³C NMR signals give a set of resonances at 194.85, 183.69, 131.91, 130.7, 129.3, 128.9, 127.75, 111.3, 77.42, 77.0, 76.5, 55.6, 46.2, 39.9, 39.6, 39.4, 39.12 and the complex at 129.8, 127.6, 126.2, 77.4, 77.0, 76.5, 39.1, 38.8, 38.2, 38.0, 37.7 and 37.45 which favours the involvement of pyridine nitrogen coordinating with the metal.

Thermal analyses of the complexes (Table-4) of I, II and III differ very much. The complex of I undergoes single stage decomposition whereas II and III undergo multistage decomposition. Thermal decomposition of the complex I proceeds with an exothermic peak at 153.4°C. At this temperature, 89.56% loss indicates the elimination of all the ligands attached to the metal atom. Complex II shows 40.9% loss of initial weight due to the elimination of BP3HA ligand over 0-125°C with an endothermic broad peak on DTA curve. The second exothermic peak of weight loss started at 192.6°C and ended at 210°C by the expulsion of 2 nitrate ligands. The third stage weight loss of 41.6% is due to the elimination of other ligands with strong exothermic peak at 380.5°C. The complex III undergoes thermal decomposition with two exothermic and two endothermic processes. The first endothermic peak with a weight loss of 40.3% over 0-120°C represents the elimination of one BP4HA ligand. The second sharp exothermic peak over 125-135°C represents some oxidation reaction by nitrate ligands. The third endothermic peak with the weight loss of 21.4% over 150-340°C corresponds to the elimination of two nitrate ligands. The fourth exothermic peak starts at 380.5°C and goes beyond 460°C due to expulsion of the remaining ligand. The stability of the complexes differs from each other.

TABLE-4
TGA ANALYSIS OF COMPLEXES

Complex	Temperature _	Weight	DTA peak	
	range (°C)	Found	Calcd.	(°C)
I	153–179	89.6	89.6	
II	0.0-125	40.9	40.8	40.8
	192-210	30.6	28.7	205.5
	380-446	41.6	40.2	391.8
III	0-110	40.3	39.9	60.2
	120-140	10.2	10.0	123.4
	150-345	21.4	27.5	296.9
	350-442	26.3	24.1	358.6

Antimicrobial activity

Antimicrobial activity of the complexes, I, II, III, IV, V and VI, ligands VII, VIII and IX and the corresponding metal salts Co(NO₃)₂ and Co(ClO₄)₂ were screened against *E. coli, K. pneumoniae, P. aeruginosa, C. albicans, S. albicans* and *S. aureus* at a concentration of 100 μg/mL by disc diffusion method¹⁵. For all the species studied (Table-5), complexes were found to be highly active and showed higher clear inhibition zone (14–24 mm) in comparison to the ligands VII, VIII and IX (4–10 mm) except for *S. aureus* which was found to give no effect (*i.e.*, growth is not retarted).

TABLE-5 ANTIMICROBIAL ACTIVITY OF THE TEST SAMPLES: DIAMETER OF ZONE OF INHIBITION

Sample	E. coli (mm)	S. aureus (mm)	K. pneumoniae (mm)	P. aeruginosa (mm)	S. albicans (mm)	C. albicans (mm)
$Co(NO_3)_2$	23.0	34.0	28.0	28.0	35.0	28.0
Co(ClO ₄) ₂	20.0	28.6	26.4	26.0	30.2	27.6
VII	13.0	14.0	12.0	2.0	16.0	15.5
VIII	12.0	8.0	7.0	4.0	12.0	14.0
IX	6.0	5.0	6.0	4.0	13.0	14.0
I	15.0		12.0	15.0	14.0	23.0
11	14.4	erene.	12.4	14.6	14.8	22.6
III	15.0	delitario	13.0	4.0	14.0	20.0
IV	14.8	Paramone.	12.8	4.4	14.6	20.4
V	19.0		15.0	16.0	16.0	22.0
VI	16.4	***************************************	14.2	15.8	15.8	22.2

The qualitative results are given in Table-5 and the quantitative results are given in Fig. 4. The microbes showing higher inhibition zone (> 8 mm radii) were selected (two bacteria, E.coli (G-), S. albicans (G+) and a fungus C. albicans) for the quantitative determination of MIC. The MICs of V, VI and IX were found to be very minimal and effective even at the concentration of 20 µg/mL to inhibit the growth of E. coli (G⁻) and S. albicans (G⁺), whereas I, II, III and IV were found to be effective at the concentration of 30 µg/mL against S. albicans (G⁺) (Fig. 4). Free salts of cobalt nitrate and cobalt perchlorate exhibited the same activity as the complexes. However, the administration of cobalt(II) free salt is not desirable due

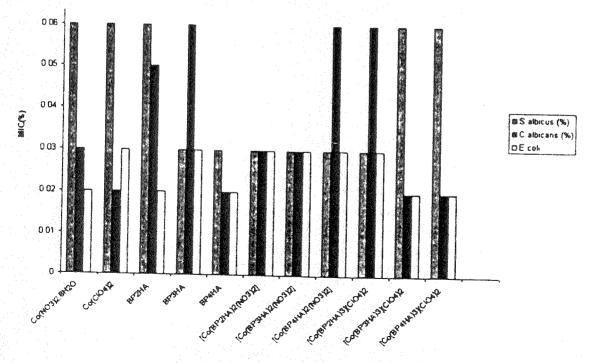


Fig. 4. Percentage of inhibition of the test samples against S. albicans, C. albicans and E. coli

to the direct interaction of biological ligands or their solubility in the serum or lipids. In the complex form, the compound will be much safer if it can show similar activities. The concentration of cobalt(II) if released under biological conditions will be of the order of $2-8\,\mu g$ from the complex, whereas the same effect is observed for 100 mg of the pure cobalt nitrate solution. The compounds with high inhibitory zone were expected to show minimal MIC. The antifungal activity study against *C. albicans* followed the expected trend whereas the antibacterial activity study against *E. coli* (G⁻) and *S. albicans* (G⁺) followed the opposite trend. This observation is due to the higher selectivity and specificity of the complex towards a particular microorganism.

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