



Synthesis, Spectral Characterization and Biocidal Studies of Copper(II) Complexes of Chromen-2-one-3-carboxy Hydrazide and 2-(Chromen-3'-onyl)-5-(aryl)-1,3,4-oxadiazole Derivatives

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Abstract: Copper(II) complexes of chromen-2-one-3-carboxyhydrazide and 2-(chromen-3'-onyl)-5-(aryl)-1,3,4-oxadiazole derivatives have been synthesized. The structural features have been determined from their microanalytical, magnetic susceptibility, molar conductance, IR, UV Vis, ¹H NMR and ESR spectral data. All the Cu(II) complexes exhibit the composition Cu(Ln)₂X₂; where L1= chromen-2-one-3-carboxy hydrazide, L2 = 2-(chromen-3'-onyl)-5-(2"-hydroxy phenyl)-1,3,4-oxadiazole, L3 = 2-(chromen-3'-onyl)-5-(4"-nitrophenyl)-1,3,4 -oxadiazole and L4 = 2-(chromen-3'-onyl)-5-(4"-chlorophenyl)-1,3,4-oxadiazole; X = Cl⁻, Br⁻, NO₃⁻, CH₃COO⁻, ClO₄⁻ and CNS⁻. The N, O donor ligands act as a bidentate ligand in all the complexes. Distorted octahedral geometry for all the Cu(II) complexes is proposed. Molecular modeling studies have been made for the rapid structure building, geometry optimization and molecular display. These complexes show the conductance values, supporting their non-electrolytic nature. The monomeric nature of the complexes was confirmed from their magnetic susceptibility values. These complexes have been screened for their antimicrobial activities against some bacterial species like *S.aureus*, *E.coli*, *Pseudomonas aeruginosa* and few fungal strains *C.albicans* and *Cryptococcus neoformans*.

Keywords: Chromene, Hydrazide, 1,3,4- Oxadiazole, Octahedral geometry, Antimicrobial

Introduction

The drugs containing a chromen-2-one nucleus have been reported in therapeutics for a wide variety of antibiotics¹, anticoagulants² and skin pigmenting agents³. Hydrazides have been investigated due to their antibacterial, antifungal, antitumour and biocidal activity⁴. Hydrazides are highly useful starting materials and intermediates in the synthesis of heterocyclic molecules⁵. Metal chelates with hydrazide derivatives have been the subject of several studies due to their structural aspects⁶. Many 1,3,4-oxadiazole derivatives show remarkable bactericidal and fungicidal activities⁷. The development of bacterial or fungal resistance to existing drugs is a major problem in anti microbial therapy and necessitates continuing research into new classes of antimicrobials⁸. The interesting properties of the metal chelates of chromen-2-one carboxy hydrazide and 1,3,4-oxadiazole derivatives have stimulated research in these compounds that find a variety of laboratory uses and many industrial applications^{9,10}. For the study and designing of drug like molecules, the structure - reactivity correlation is very important¹¹. In order to develop new compounds of high potency, the biologically important moieties have been coupled and with the resulting molecules, metal chelates were synthesized and characterized.

Experimental

All chemicals used were of A.R. grade. The metal salts were prepared and analysed following the standard procedures¹². The analyses for metal and anions were carried out by known methods¹². Copper was estimated iodometrically by titration, chloride by Volhard's method, perchlorate by Kurz's method and acetate and nitrate by elemental analysis. C, H, N analyses were performed by microanalytical unit, CDRI, Lucknow. IR spectra were recorded on a Perkin-Elmer 783 IR-spectrophotometer. UV-Vis spectra of the complexes were recorded on Perkin-Elmer Lambda-25 spectrophotometer. The ¹H NMR spectra were recorded on a Bruker DRX-300 spectrometer at SAIF, Lucknow. The X-band ESR spectra of the complexes were recorded at room temperature in solid state in a Varian E112 X/Q band ESR- spectrometer at IIT Madras. Magnetic susceptibility was measured by vibrating sample magnetometer at IIT Madras.

Conductivity measurements were made on a Systronics direct reading conductivity meter. Molecular modeling studies were carried out in computer, 3D MAX, MAYA professional version at Bangalore. Antimicrobial studies were also carried out from sree chithra thirunal institute for medical sciences and technology, thiruvananthapuram.

Synthesis of ligands

Chromen and its derivatives were synthesized by Pechmann reaction method¹³. All the ligands (L1, L2, L3 and L4) were prepared using the methods reported earlier¹⁴. 3-Ethyl carboxy coumarin ester was prepared by condensation of salicylaldehyde with diethyl malonic ester using conc. H₂SO₄ according to Pechmann reaction¹³. The compound obtained above (14 mmole) and hydrazine hydrate (16 mmole) were dissolved in a sufficient quantity of ethanol to give a clear solution and refluxed for 3 h. The contents were concentrated to a small volume. On cooling, the crystals of chromen-2-one-3-carboxy hydrazide (L1) separated out which were filtered and recrystallized from ethanol to give TLC pure colourless needles¹⁵.

Ligands, 2-(chromen-3'-onyl)-5-(2''-hydroxy phenyl)-1,3,4-oxadiazole [L2], 2-(chromen-3'-onyl)-5-(4''-nitrophenyl)-1,3,4-oxadiazole [L3] and 2-(chromen-3'-onyl)-5-(4''-chlorophenyl)-1,3,4-oxadiazole [L4] were synthesized by condensing chromen-2-one-3-carboxy hydrazide with salicylic acid, *p*-nitro benzoic acid and *p*-chloro benzoic acid respectively¹⁵.

Chromen-2-one-3-carboxy hydrazide (10 mmole) in phosphorous oxychloride (15 mL) and the acids [salicylic acid or *p*-nitro benzoic acid or *p*-chloro benzoic acid] (10 mmole) were added into a 100 mL R.B. flask. The reaction mixture was refluxed for 5 h, cooled to room temperature and poured on to crushed ice. On neutralization with 2% NaHCO₃ solution, a solid mass separated out, which was filtered, washed with water and recrystallized from methanol to give L2 or L3 or L4 which were purified by TLC. The melting point of the four ligands were L1=136 °C, L2=310 °C, L3=203 °C and L4=138 °C. All the ligands were confirmed by m.p.ts, IR and ¹H NMR spectra.

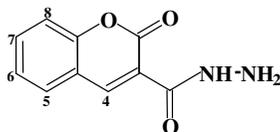


Figure 1. Chromen-2-one-3-carboxy hydrazide (L1); m.p. 136°

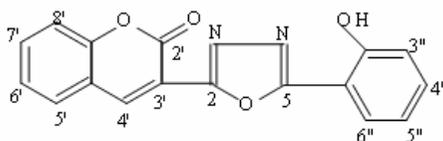


Figure 2. 2-(Chromen-3'-onyl)-5-(2''-hydroxy phenyl)-1,3,4-oxadiazole (L2); m.p. 310°

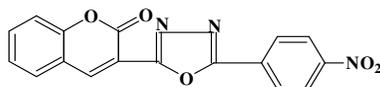


Figure 3. 2-(Chromen-3'-onyl)-5-(4''-nitrophenyl)-1,3,4-oxadiazole (L3); m.p. 203°

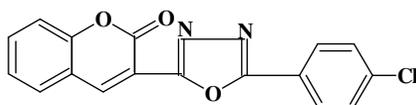


Figure 4. 2-(Chromen-3'-onyl)-5-(4''-chlorophenyl)-1,3,4-oxadiazole (L4); m.p.138°

Synthesis of complexes

Copper(II) metal salts with different anions were freshly prepared from EMerck grade CuCO₃ and using 1:1 respective acids. The solution of 1 mmole of metal salt (*e.g.* Cu(NO₃)₂·3H₂O, 242 mg) in ethanol was mixed with ethanolic solution of 1 mmole of the ligands (L1= 204 mg, L2=306 mg, L3= 335 mg or L4 = 324 mg) and refluxed for 2-3 h. Volume of the solution was then reduced by keeping on a hot water bath and after cooling, pH of the mixture was raised to ~7.2 with one or two drops of alcoholic ammonia solution. The metal complexes that precipitated were filtered, washed with ethanol and dried in a desiccator over anhydrous calcium chloride.

Results and Discussion

Analytical data given in Table 1 suggest that the metal-ligand stoichiometry is 1:2 and the complexes are monomeric in nature. Molar conductivity data obtained in methanol, acetonitrile and nitrobenzene suggest that all the complexes are of non-electrolyte type^{16,17}. All the Cu(II) complexes are greenish brown or greenish grey in colour. These complexes are stable in air and insoluble in H₂O, slightly soluble in ethanol and methanol and very well soluble in chloroform, nitrobenzene and dimethylformamide.

Table 1. Analytical, magnetic and electronic spectral data of Cu(II) chromen-2-one-3-carboxy hydrazides and 1,3,4-oxadiazoles

Complex	Colour	Yield %	Analyses Calcd (Found), %				Magnetic susceptibility μ_{eff} in BM	UV-vis bands in cm^{-1}
			Cu	C	H	N		
Cu(L1) ₂ Cl ₂	Dark greenish brown	80	11.78 (11.79)	41.19 (41.20)	2.94 (2.95)	10.31 (10.32)	1.89	15384 d-d, 24390 CT
Cu(L1) ₂ Br ₂	Greenish brown	85	10.12 (10.13)	37.97 (37.98)	2.52 (2.53)	8.86 (8.86)	1.95	15672 d-d, 24589 CT
Cu(L1) ₂ (NO ₃) ₂	Yellowish brown	77	10.73 (10.74)	40.26 (40.27)	2.68 (2.68)	14.08 (14.09)	1.91	16000 d-d, 25000 CT
Cu(L1) ₂ (Ac) ₂	Greenish brown	75	10.84 (10.85)	48.81 (48.80)	3.72 (3.73)	9.49 (9.49)	2.01	16160 d-d, 25547 CT
Cu(L1) ₂ (ClO ₄) ₂	Greenish grey	85	9.53 (9.54)	35.76 (35.77)	2.37 (2.38)	8.34 (8.35)	1.99	15583 d-d, 25520 CT
Cu(L1) ₂ (CNS) ₂	Greenish brown	79	8.5 (8.45)	54.6 (54.59)	2.67 (2.68)	7.49 (7.50)	1.92	16130 d-d, 23126 CT
Cu(L2) ₂ Cl ₂	Yellowish brown	70	7.59 (7.58)	48.8 (48.79)	2.39 (2.38)	6.69 (6.70)	1.94	16124 d-d, 24780 CT
Cu(L2) ₂ Br ₂	Dark greenish brown	74	7.93 (7.92)	51.1 (51.2)	2.5 (2.49)	10.5 (10.51)	1.90	16142 d-d, 24478 CT
Cu(L2) ₂ (NO ₃) ₂	Greenish brown	82	7.99 (7.97)	57.4 (57.35)	3.27 (3.26)	7.05 (7.10)	1.91	16098 d-d, 24343 CT
Cu(L2) ₂ (Ac) ₂	Dark greenish brown	80	7.25 (7.26)	46.62 (46.63)	2.28 (2.29)	6.4 (6.39)	1.98	16154 d-d, 24876 CT
Cu(L2) ₂ (ClO ₄) ₂	Light brown	75	7.95 (7.96)	50.68 (50.67)	2.23 (2.24)	10.43 (10.42)	1.94	15779 d-d, 24780 CT
Cu(L2) ₂ (CNS) ₂	Greenish brown	79	7.10 (7.11)	45.63 (45.64)	2.01 (2.01)	9.39 (9.40)	1.89	15698 d-d, 24768 CT
Cu(L3) ₂ Cl ₂	Greenish grey	78	7.45 (7.46)	47.55 (47.54)	2.09 (2.08)	13.05 (13.11)	1.92	15723 d-d, 24457 CT
Cu(L3) ₂ Br ₂	Yellowish grey	81	7.51 (7.51)	53.5 (53.52)	2.81 (2.82)	9.85 (9.86)	2.01	15684 d-d, 24226 CT
Cu(L3) ₂ (NO ₃) ₂	Greenish brown	75	6.85 (6.86)	43.72 (43.74)	1.92 (1.93)	9.01 (9.02)	1.99	15720 d-d, 24768 CT
Cu(L3) ₂ (ClO ₄) ₂	Dark greenish brown	74	8.16 (8.15)	52.02 (52.05)	2.29 (2.3)	7.14 (7.15)	1.97	16139 d-d, 25160 CT
Cu(L3) ₂ (Ac) ₂	Greenish brown	70	7.33 (7.34)	46.73 (46.72)	2.06 (2.07)	6.41 (6.40)	1.91	16152 d-d, 24453 CT
Cu(L3) ₂ (CNS) ₂	Yellowish brown	75	7.64 (7.65)	48.74 (48.74)	2.15 (2.16)	10.03 (10.04)	1.90	16124 d-d, 24640 CT
Cu(L4) ₂ Cl ₂	Greenish brown	80	7.70 (7.71)	54.87 (54.86)	2.94 (2.95)	6.73 (6.74)	2.01	16156 d-d, 24682 CT
Cu(L4) ₂ Br ₂	Greenish grey	70	7.01 (7.02)	44.73 (44.73)	2.52 (2.53)	6.14 (6.15)	1.95	16157 d-d, 24786 CT
Cu(L4) ₂ (NO ₃) ₂	Dark greenish brown	75	11.78 (11.79)	41.19 (41.20)	2.68 (2.68)	10.31 (10.32)	1.89	16029 d-d, 24425 CT
Cu(L4) ₂ (ClO ₄) ₂	Greenish brown	79	10.12 (10.13)	37.97 (37.98)	3.72 (3.73)	8.86 (8.86)	1.95	15732 d-d, 25321 CT
Cu(L4) ₂ (CNS) ₂	Yellowish brown	75	10.73 (10.4)	40.26 (40.27)	2.37 (2.38)	14.08 (14.09)	1.91	16000 d-d, 24992 CT

¹H NMR spectra

The four ligands L1, L2, L3 and L4 were characterized by ¹H NMR spectroscopy, at a frequency 300 MHz. The ¹H NMR spectral data are given in Table 2. The ¹H NMR spectral data confirms the reported ligands¹⁴.

Table 2. The ¹H NMR spectral data of the ligands

Ligand	δ Values, ppm	Nature of signal	Corresponding proton
L1	6.98	m, 2H	H-6, H-8
	7.40	m, 1H	H-7
	7.69	m, 1H	H-5
	8.14	s, 1H	H-4
	8.43	s, 1H	CONH
	8.61	s, 2H	NH ₂
L2	7.13	m, 4H	H-6',H-8',H-3'',H-5''
	7.91	m, 4H	H-5',H-7',H-4'',H-6''
	8.10	s, 1H	H-4'
L3	7.21	m, 2H	H-6',H-8'
	7.52	d, 2H	H-3'',H-5''
	7.67	m, 1H	H-7'
	7.83	m, 1H	H-5'
	8.10	s, 1H	H-4'
	8.15	d, 2H	H-2'',H-6''
L4	7.44	m, 3H	H-6',H-7',H-8'
	7.86	d, 1H	H-5'
	8.05	s, 1H	H-4'
	8.12	m, 4H	H-2'', H-3'',H-5'', H-6''

Electronic spectra

The electronic spectra in methanolic solution were taken in the range 11111 to 50000 cm⁻¹ and the absorption bands along with their assignments are given in Table 1. Cu(II) is a typical case where strong Jahn Teller distortion prevents the formation of regular octahedral complexes. The electronic spectra of the present copper(II) complexes show a broad band with a maximum of ~16160 cm⁻¹. This band may be due to the square planar or tetragonally distorted octahedral geometry around Cu(II)¹⁸. The band is likely to be the result of combination of ²B_{1g} → ²A_{1g}, ²B_{1g} → ²B_{2g} and ²B_{1g} → ²E_{1g} transitions in D_{4h} symmetry¹⁹. The high intensity band observed around ~24000 cm⁻¹ for all the complexes in the u.v. region may be assigned to a ligand to metal, charge transfer excitation.

Magnetic moment

The effective magnetic moments of the Cu(II) complexes at room temperature are also shown in Table 1. The magnetic moment measurements indicate that the Cu(II) complexes are paramagnetic and the magnetic moment values are close to the spin only value of 1.73 BM, expected for one unpaired electron of a d⁹ configuration²⁰. According to Lewis and Walton the octahedral complexes of copper(II) have room temperature moments in the range of 1.9 to 2.0 BM²¹. Planar complexes have as high a moment as 2.2 BM at room temperature, although distortion would appreciably reduce it if the low symmetry ligand fields produced are large, compared to spin-orbit coupling²². The magnetic moments for the present Cu(II) complexes vary from 1.89 to 2.01 BM suggestive of octahedral coordination.

IR spectra

The IR spectral bands and their assignments for the important groups of the free ligands and the complexes are helpful in deciding the stereochemical environment around Cu(II) ion in the complexes. The IR spectrum of the ligand L1 shows bands at 3458 and 3305 cm^{-1} , which are assigned to the two >NH stretching vibrations of the carboxy hydrazide group²³. The band at 3458 cm^{-1} due to -NH stretching vibration of the terminal -NH₂ group is unaffected in the complexes, indicating the non-coordination of -NH₂ group to the metal atom²³. The significant band in ligand (L1) undergoing change on complexation is that at 3305 cm^{-1} representing the stretching mode of hydrazide >NH group. This band is shifted by around 45-60 cm^{-1} to lower frequencies in the complexes confirming its involvement in co-ordination. Also, the bands at 1526 cm^{-1} and 731 cm^{-1} representing the in-plane and out-of-plane bending modes of >NH group show pronounced downshift ($\sim 30 \text{ cm}^{-1}$) in the complexes²⁴. The ligand spectrum exhibits two bands occurring at 1700 cm^{-1} and 1650 cm^{-1} , which may be due to the ring carbonyl ($\nu_{\text{C=O}}$, coumarin) and hydrazide carbonyl stretching frequencies. On chelation, the ring carbonyl band is red shifted by 30-40 cm^{-1} and the other carbonyl band is unaffected. The appearance of bands at 1272, 1156, 1030 and 980 cm^{-1} in the spectrum of Cu(II) complexes of chromen-2-one-3-carboxy hydrazide suggests the bidentate nature of the ligand²³.

IR spectra of the ligands L2, L3 and L4 exhibit a strong band at 1710 cm^{-1} representing the $\nu_{\text{C=O}}$ chromen carbonyl group. On chelation this band is shifted to lower frequencies ($\sim 20\text{-}40 \text{ cm}^{-1}$) showing its involvement in complexation²⁵.

The significant band around 3580 cm^{-1} representing the oxadiazole ring stretching frequency is highly altered and shifted to about 40-50 cm^{-1} to lower frequencies in the oxadiazole containing complexes²⁶. This is further confirmed by the bands at 1600 cm^{-1} and 840 cm^{-1} representing the in-plane and out-of-plane bending modes of $\nu_{\text{C=N}}$ group in the oxadiazole ring showing pronounced downshift $\sim 30 \text{ cm}^{-1}$ in the complexes²⁶.

The bands around 1480, 1370, 1030 and 970 cm^{-1} are assigned to the oxadiazole ring (nucleus) vibrations²⁶. The bands at 1030 cm^{-1} can be assigned to $\nu_{\text{C-O}}$ and the bands in the region 970-945 cm^{-1} are assigned to $\nu_{\text{(N-N)}}$ groups. A strong band around 820 cm^{-1} representing the stretching mode of the disubstituted benzene is also present in all the oxadiazole ligands and their Cu(II) complexes. These bands are unaffected in the complexes, showing their non-involvement in complexation²⁷. The bands around 530 and 480 cm^{-1} are assigned to $\nu_{\text{(M-N)}}$ and $\nu_{\text{(M-O)}}$ modes respectively²⁸. The appearance of bands at 1404, 1313, 1071 and 982 cm^{-1} in the spectrum of Cu(II) complexes of 2 (chromen-3'-onyl)-5-(aryl)-1,3,4-oxadiazole suggests the bidentate nature of the ligand²⁸.

The bands at 1422 cm^{-1} and 1312 cm^{-1} assigned to ν_2 vibration of coordinated nitrate in the complex²⁹. The spectrum of the perchlorate complex shows strong bands at 1147 (ν_3) and 621 cm^{-1} (ν_4) with pronounced splitting³⁰. In the IR spectra of Cu(II) acetate complex, strong bands appear at 1570 cm^{-1} and 1395 cm^{-1} assignable to coordinated acetate group vibrations³¹. The thiocyanate complex of Cu(II) shows a strong band at 2040 cm^{-1} along with medium bands at 828 and 460 cm^{-1} indicating N-coordinated thiocyanate in the complex³². The univalent nature of the halide ion evidenced by IR spectra of the chloride complexes and their non-electrolyte nature suggest that the chloride ion is coordinated to the metal³³.

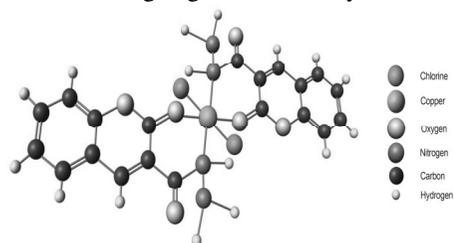
ESR spectra

The x-band ESR spectrum of Cu(L3)₂Cl₂ complex recorded at 300K, at a microwave frequency 9.33 GHz with a field strength of 4000G, is characteristic of copper(II) in axial field symmetry, $g_{\parallel} = g_z$ and $g_{\perp} = g_x = g_y$. Calculated values of g_{\parallel} and g_{\perp} are 2.215 and 2.08

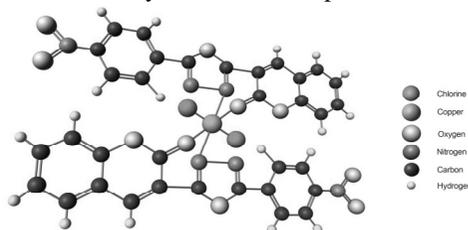
respectively. The trend $g_{\parallel} > g_{\perp} > g_e$ (free ion value) observed for this complex shows that the unpaired electron is located in the $d_{x^2-y^2}$ orbital of the copper(II) ion and the spectrum obtained is characteristic of axial symmetry³⁴. A_{\parallel} value calculated for the complex is $200 \times 10^4 \text{ cm}^{-1}$ since the hyperfine component shows no hyperfine split; $A_{\perp} = 0$ ³⁵. From the observed value, it is clear that $g_{\parallel} > g_{\perp} > 2.00$ and $A_{\parallel} > A_{\perp}$ which suggests that the complex is present in distorted octahedral geometry. Molecular orbital coefficients, α^2 (covalent in-plane σ -bonding) and β^2 (covalent in-plane π -bonding) were calculated and it is found that $\alpha^2 > \beta^2$ which shows that the σ -bonding is more covalent than that of the in-plane π -bonding³⁶.

Molecular modeling studies

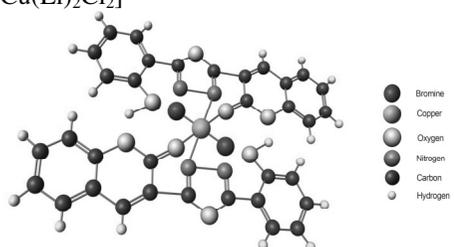
Molecular modeling studies are carried out in computer, using 3D MAX software and energy minimized configurations are shown below. To describe the physical, chemical and biological properties, the structure is very important. For the study of the binding modes of drug like molecules and for the designing of molecular systems, the structure - reactivity correlation is important.



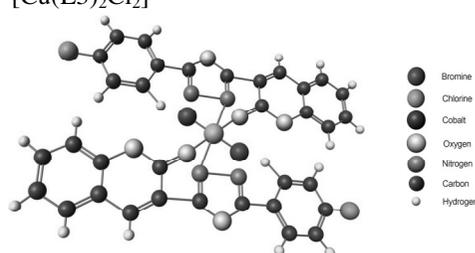
Energy minimized configuration for [Cu(L1)₂Cl₂]



Energy minimized configuration for [Cu(L3)₂Cl₂]



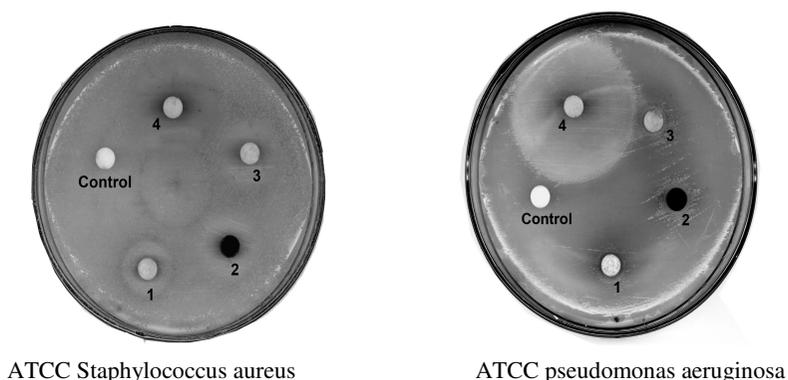
Energy minimized configuration for [Cu(L2)₂Br₂]



Energy minimized configuration for [Cu(L4)₂Br₂]

Antimicrobial activity

Carboxy hydrazide of chromen-2-one and 2-(chromen-3'-onyl)-5-(aryl)-1,3,4-oxadiazole derivatives and their Cu(II) metal complexes were screened for antibacterial activity and antifungal activity against the bacterial strains *S. aureus*, *E. Coli* and *Pseudomonas aeruginosa* and the fungal strains *C. albicans* and *Cryptococcus neoformans* by disc diffusion technique. The test solutions were prepared in DMSO and DMF at different concentrations (50-500 $\mu\text{g/mL}$). Chloromycetin and Amphotericin B discs were used as standard drugs for evaluating the antibacterial and antifungal activity. Nutrient agar was used as culture medium. The zones of inhibition formed were measured in mm. Cu(II) metal complexes were found to be more active than their ligands. In general, metal complexes are more active than their ligands because the metal complexes may serve as a vehicle for activation of ligands as the principal cytotoxic species³⁷. The results of the biological activities show that these complexes are very active and so they can be used as drugs against the above mentioned bacterial and fungal diseases. Table 3 below shows the antimicrobial data of few Cu(II) complexes.

**Figure 5.** Antimicrobial activity**Table 3.** Antimicrobial activity of Cu(II) complexes (Zone of inhibition in mm)

Complex	<i>S.aureus</i>	<i>E.coli</i>	<i>P.aeruginosa</i>	<i>C.albicans</i>	<i>Cryptococcus</i>
Cu(L1) ₂ Br ₂	17	12	16	10	12
Cu(L1) ₂ (ClO ₄) ₂	21	16	22	21	20
Cu(L2) ₂ Cl ₂	18	15	12	14	17
Cu(L2) ₂ (CNS) ₂	36	20	25	16	12
Cu(L3) ₂ (NO ₃) ₂	20	18	11	17	19
Cu(L3) ₂ (Ac) ₂	10	19	27	9	18
Cu(L4) ₂ (ClO ₄) ₂	17	14	21	22	25
Cu(L4) ₂ Cl ₂	18	30	20	18	16
DMF control	[10 micro litres per disc]				

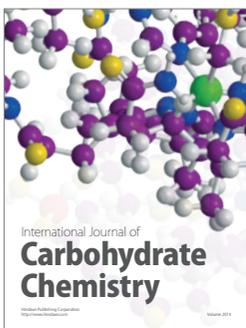
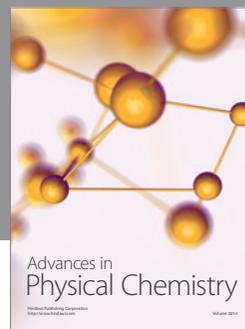
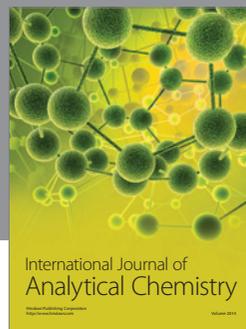
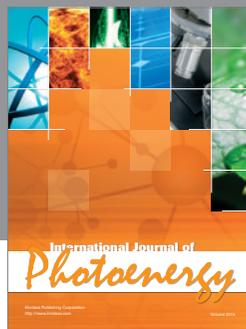
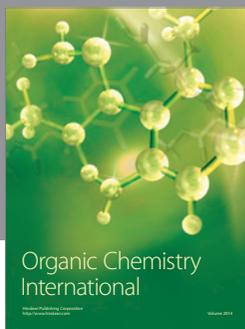
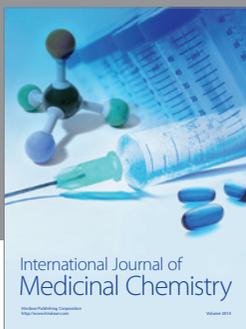
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