

New Mn(II), Co(II), Ni(II) and Cu(II) homoleptic complexes with 6-chloro-5-7-dimethyl-4oxo-4H-chro mene-3-carbaldehydes and its heteroleptic complexes with quinoline-8 ol: synthesis, characterization and antimicrobial activity

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Abstract

In the present study, the synthesis of ligand 6-chloro-5-7-dimethyl-40xo-4H-chromene-3-carbaldehydes by three steps from the substituted phenol. The formed product in the first step was further processed by fries rearrangement reaction and subsequently Vilsmeier-Haack reaction. Then, its homoleptic and heteroleptic complexes with Mn(II), Co(II), Ni(II) and Cu(II) metal ions by using second ligand quinolin-8-ol were synthesized. The ligand and complexes were characterized by different techniques, such as electron dispersive spectroscopy and elemental analysis (CHN), Fourier transform infrared (FTIR), electronic spectroscopy and magnetic susceptibility, ¹H-Nuclear magnetic resonance spectroscopy and mass spectra of ligand, electron spin resonance (ESR), thermogravimetric analysis, powder X-ray diffraction, scanning electron microscopy (SEM) and molar conductivity. The spectroscopic analysis like NMR and the FTIR shows that the both ligands are bidentate in nature. The UV-visible spectra show the homoleptic complex of Cu(II) shows square planer, while M=Ni(II), Co(II) and Mn(II) shows octahedral in nature. While the complexes with heteroleptic ligands from square planer geometry with Cu(II) and Ni(II) while Co(II) and Mn(II) show octahedral geometries. The geometry was also supported by magnetic susceptibility and FTIR spectra. The ESR spectra of Cu(II) complexes shows both are square planer geometry and the G-value was more than 4 indicating the absence of exchange interaction between Cu(II) metal ions in the solid state. The powder X-ray diffraction was used to determine the crystal system of all the complexes, while supporting to this X-ray diffraction the SEM was also taken for the nanostructure of complexes was developed or not. Then, the solution state conductivity of the complexes shows electrolytic in nature. Further, these complexes were evaluated for its antimicrobial activity by agar

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well diffusion method and structure–activity relationship. The ligands show antimicrobial activity against *S.typhi*. The Ni(II) does not show antibacterial activity, while complexes Cu(II), Co(II) and Mn(II) shows good activity against the gram-positive and the gram-negative bacteria. The heteroleptic ligand complex (6) of Cu(II) shows higher antifungal activity as compared with Ni(II), Co(II) and Mn(II) complexes.

Keywords Chromones derivatives metal complexes · EPR · TGA · Antimicrobial

Introduction

This is a trend in coordination chemistry to synthesize the heteroleptic ligand complexes. In this study, the bidentate heterocyclic ligands contain donor atom N, O and O, O was selected for synthesis of the complexes. The organic heterocyclic compounds such as flavonoids and the famous ligand quinolin-8-ol. The flavonoids are the naturally occurring heterocyclic compound can be synthesized by a previous reported method [1, 2] and from which the inorganic coordination complexes can be prepared. The substituted chromones were naturally present in different parts of the plants. The most of substituted chromones shows biological activities [3]. The activity included antibacterial, antitumor, antifungal, antioxidant, antialergic, antiviral, anti-inflammatory and anticancer activities [4, 5]. The chromones are synthesized by the cyclodehydration of 1-(O-hydroxyaryl)- 1,3 diketones or by Vilsmeier-Haack reaction [5]. We are interest in the synthesis of 3-formyl chromones derivatives because of their pharmaceutical and chemical importance [6]. They form coordination complex with transition metal ion. They form attractive intermediates which may lead to form the complexes [7]. The literature survey show that there is work found to be done on chromone metal-chelate complexes but not on the mixed ligands complexes. Therefore, we are interest in the coordination complexes of chromones with transition metal ion like Mn(II), Co(II), Ni(II) and Cu(II) ion as well as its heteroleptic ligand complexes with quinolin-8-ol.

Mixed-ligand complexes have attracted a considerable interest as a result of their vital function in biological processes. Several papers have reported synthesis and spectral characterization of mixed-ligand complexes as well as their potential applications [8, 9]. It was reported that the presence of heterocyclic nitrogen donor ligands including N, N-donor such as 1, 10-phenanthroline or N, O-donor such as 8-hydroxyquinoline or glycine lead to a significant improvement of the biological and pharmacological properties of the complexes [10–17]. The some of the metal-chromone complexes show the antimicrobial activity was checked by well diffusion methods, and the inhibition zone was measured in mm-scale [18–20].

Experimental

Materials and methods

Metal salts like NiCl₂. $6H_2O$, CuCl₂. $2H_2O$, CoCl₂. $6H_2O$, MnCl₂. $5H_2O$ (99.90%, Merck) quinolin-8-ol, POCl₃ (99.98%, Merck), dry Pyridine, anhydrous AlCl₃ (99.98%, Merck) ethanol, methanol, DMSO, DMF, chloroform and acetic acid (98.99%, Merck) were used as it is for synthesis of ligand and its metal complexes.

A melting point of the synthesized organic ligands was determined on digital melting point/boiling Point apparatus EQ-730 equiptronics and is uncorrected. Elemental analyses of C, H and N were done on a JEOL C, H and N elemental analyzer at the SAIF, Indian Institute of Technology (IIT-Powai), Mumbai University and the SEM and EDS from department of physics Savitribai Phule Pune University Pune. The electronic spectra for ligands and complexes were recorded on UV-1800 Shimadzu spectrophotometer in the range 200-800 nm. The electronic spectra of all the complexes were taken at 10^{-3} M concentration in the DMSO and DMF solution. The magnetic susceptibility was recorded on Gouy balance method at room temperature by using Hg $[Co(SCN)_4]$ as the calibrate. The FTIR spectra (KBr Pellets) were measured on IRAffinity-1 Shimadzu FTIR spectrophotometer in the range 4000-400 cm⁻¹. ¹H NMR spectral measurements were performed on Bruker AscendTM 500 MHz spectrometer. The reported chemical shifts were against TMS; DMSO d_6 solvents were used for chromone derivative ligand at Department of Chemistry, Savitribai Phule Pune University. LC-MS measurements of organic ligand were performed on UHPLC-Ultimate-3000; thermo scientific LC-MS spectrometer at Department of Chemistry, Savitribai Phule Pune University was used for characterization. ESR spectra were obtained from JEOL Japan JES FA200 ESR spectrometer with X-band at room temperature. The ESR spectra obtained from SAIF, IIT Powai University of Mumbai. The thermal analysis was measured from room temperature to 1000 °C in air and cobalt complexes in nitrogen atmosphere heated at non-isothermally with heating rate 10 °C/min. Using TGA-50 Shimadzu thermogravimetric analyzer. The powder X-ray diffraction studies of complexes were taken for determination of crystal structure of complexes. The molar conductance of complexes was recorded on an Elico conductivity bridge in DMF 10⁻⁴ M solution using a dip-type conductivity cell fitted with a platinum electrode.

Synthesis of Ligand: 6-chloro 5, 7 dimethyl-4oxo-4H-chomene-3- carbaldehyde

The ligand 6-chloro 5, 7 dimethyl-40x0-4H-chomene-3- carbaldehyde was synthesized by the Vilsmeier–Haack reaction [21, 22]. The synthesis of 6-chloro 5, 7 dimethyl-40x0-4H-chomene-3- carbaldehyde derivative was performing by three steps. The first step is the synthesis of 4-chloro-3, 5, dimethyl phenyl acetate (Scheme 1a) from 1 mol of 4-chloro-3, 5 dimethyl phenols by reacting with 1.15 mol acetic anhydride in the presence of 5 mL dry pyridine by reported method (Schemes 2 and 3).



(a) 4-chloro-3,5-dimethylphenyl acetate





(c) 6-chloro-5,7-dimethyl-4-oxo-4 H-chromene-3-carbaldehyde

Scheme 1 Synthetic route for ligand (L2)

The second step is fries rearrangement reaction for preparation of acetophenone derivative that is 1(3-chloro-6-hydroxy-2, 4 dimethyl phenyl) ethanone (**b**) from 4-chloro-3, 5, dimethyl phenyl acetate (a) by using 1.25 mol of anhydrous AlCl₃ in large one neck round bottom flask attach with air condenser. Then, in it adding the 1 mol of aryl acetate rapidly. The exothermic reaction occurs with evolution of HCl gas. After complete evolution of HCl gas, the whole reaction mixture kept in oil bath and reflux it at temperature in between 140 $^{\circ}$ C and 150 $^{\circ}$ C for 2 h. Then, the reaction mixture allowed standing for overnight. The complex thus formed was broken by adding ice-cold water in round bottom flask. The separated



Scheme 2 Synthesis route of M-L2 complexes

product was filtered and recrystallized from aqueous alcohol. This is a Fries reaction (Scheme 1. Step-II (b)) by literature method [23, 24].

The last step is the synthesis of 6-chloro-5-7-dimethyl-4oxo-4H-chromene-3-carbaldehyde by taking the 25 mL dimethylformide and 15 mL POCl₃ in round bottom flask with constant stirring by using magnetic needle. The whole reaction mixture was kept in ice bath then adding 15 mL POCl₃ drop wise. The whole reaction mixture was stirred on magnetic stirrer for about 1 h to get pink formylating complex [25]. Then, 0.05 mol of product (**b**) dissolved in minimum amount of DMF. Then, it was added into the pink formylating complex maintaining temperature of the mixture below 20 °C. Then, reaction mixture was stirred for 2 h. The reaction mixture was allowed to stand at room temperature for overnight. The reaction mixture was poured into the crushed ice with vigorous stirring. The product (**c**) was precipitated as yellow solid of 6-chloro 5,7dimethyl-4-oxo-4H-chomene-3-carbaldehyde, filtered and recrystallized from acetic acid: ethanol (1:1ratio) (Scheme 1. Step-III (c).



Scheme 3 Synthetic route of heteroleptic complexes

Synthesis of the homoleptic complexes

Synthesis of Ni(II), Cu(II), Co(II) and Mn(II) complexes with 6-chloro-5,7 dimethyl-4-oxo-4H-chremene-3-carbaldehyde

Synthesis of Ni(II) complex: $[C_{24} H_{22} Cl_4 NiO_8]$ (1) The complex Ni(II) was synthesized by adding methanolic solution of nickel chloride hexahydrate (0.118 g, 1 mol) to a methanolic (10 mL) solution of 6-chloro-4-oxo-4H-chromene-3-carbaldehyde (I) (0.236 g, 2 mol) in the presence of 2–3 drops of acetic acid with vigorous stirring. Then, this solution was reflux at 80–90 °C for 12 h. After 12 h of refluxing, the solution was kept for overnight. The color of the solution change occurs from green to orange. Then, 2–3 drops of distilled water were added the complex get solidify with dark orange colored, after which the orange colored solid was filtered and air dried. The weight of product was 0.427 g, (78.20%).

Synthesis of Cu (II) complex: $[C_{24}H_{18}Cl_4CuO_6]$ (2) The ligand 0.225 g. of 6-chloro-5, 7 dimethyl-3-formyl-chromenes was dissolved in 25 mL acetic acid: methanol (1:1) and was refluxed. To this refluxed ligand solution, 25 mL methanolic solution of CuCl₂.2H₂O (2.02 g, 1 mol) was added drop by drop with continuous stirring, and the resulting reaction mixture was further refluxed for 3 h and allow to stand

for overnight. The dark olive green solid was separated out, and it was filtered and washed with methanol. The complex was dried at room temperature in vacuum.

Synthesis of Co(II) complexes: $[C_{24}H_{22}Cl_4CoO_8]$ (3) The recrystallized ligand 6-chloro-5-7-dimethyl-40x0-4H-chomene-3-carbaldehyde (0.11 g, 2 mol) was dissolved in 10 mL methanol with acetic acid. The cobaltous chloride (0.238 g, 1 mol) was dissolved in 10 mL methanol. The ligand solution was added into Co(II) salt solution with constant stirring. The whole mixture was refluxed for 8 hat temperature 60–80 °C. The color of the solution became dark red. The solution was evaporated up to the near dryness. The complex was filtered and dried in vacuum. The whole reaction was carried out in inert medium.

Synthesis of Mn(II) complexes: $[C_{24}H_{22}Cl_4MnO_8]$ (4) The methanolic solution in the presence of acetic acid (10 mL) of 6-chloro- 5-7-dimethyl-40x0-4H-chomene-3-carbaldehyde (2 mmol, 0.238 g) was added drop wise to a stirred water-methanol (1:1, 10 mL) solution of Mn(II) salt (1 mmol). The mixture was refluxed with constant stirring for 6 h at 60–80 °C temperature. The solution was cooled overnight at room temperature. The precipitated complex was filtered off, washed several times with cold methanol and dried at room temperature.

Synthesis of heteroleptic ligand complexes of quinolin-8-ol and 6-chloro- 5-7-dimethyl- 4-oxo-4H-chomene-3-carbaldehyde with Ni (II), Cu (II) and Co (II) metal ions

Synthesis of Ni(II) complexes: $[C_{21}H_{15}Cl_2NNiO_4]$ (5) The mixture of 10 mL methanolic solution of NiCl₂.6 H₂O (0.237 g, 1 mol), and 10 mL methanolic solution in the presence of acetic acid of 6-chloro- 5-7-dimethyl-40xo-4H-chomene-3-carbaldehyde (0.236 g, 1 mol) and quinolin-8-ol (0.145 g, 1 mol) was added slowly at temperature 90–100 °C. The time to time methanol was added into the reaction mixture. The pH 8–9 was adjusted by addition of sodium hydroxide. Then, after some time the complexes get solidify. Then, the solution was filter and washed with methanol and dried in air.

Synthesis of Copper complex: $[C_{21}H_{15}Cl_2CuNO_4]$ (6) The heteroleptic ligand complex of 6-chloro-5-7-dimethyl-40xo-4H-chomene-3-carbaldehyde (0.472 g 2 mol) and quinolin-8-ol (0.290 g, 2 mol) was dissolved in 10 mL hot methanol and acetic acid. The methanolic solution of copper chloride (0.340 g, 2 mol) was added into the ligand solution. Then, whole mixture was refluxed for 4 h to get precipitate of complex. The solution was filtered through Buchner funnel and washed with cold methanol and dried in vacuum.

Synthesis of Cobalt complex: $[C_{21}H_{19}Cl_2CoNO_6]$ (7) To a methanolic solution, the dehydrated complex (3) was added into the methanolic solution of the quinolin-8-ol. The mixture was refluxed for 10–12 h to get the brown colored solid. The solid was filtrated and washed with methanol and dried into the vacuum. During the preparation of complex, the nitrogen gas was bubbled in the reaction mixture to prevent the oxidation of Co(II) into Co(III).

Synthesis of Mn(II) complex: $[C_{21}H_{19}Cl_2MnNO_6]$ (8) The 10 mL methanolic: acetic acid solution of L2 (0.238 g, 1 mol) was added with stirring to a 10 mL solution containing Mn(II) metal ion (0.158 g 1 mol) to get brown colored solution. To this resulting solution, a 10 mL methanolic solution of quinolin-8-ol was added with stirring which yielded reddish brown solid. The solid was filtrated, washed with methanol and dried in vacuum.

Antimicrobial activity study

Antibacterial activity of newly synthesized compounds was tested against the bacterial strains, Salmonella Typhi and Bacillus subtilis by a agar well diffusion method reported earlier [26]. In this method, petri dishes containing 20 mL of nutrient agar medium were spread with 100 μ L of bacterial suspension (≈ 1 O.D.). The wells of 9 mm diameter were prepared on the nutrient agar plates with the help of a sterile cork borer. The test compounds were diluted appropriately, and 100 µL of each diluted compounds was (100 µL) added into different wells, separately. The plates were allowed to diffuse at 4 °C for 10 min. Further, all plates were incubated at 37 °C for 24 h and observed for zone of growth inhibition. The obtained zones of inhibition were compared with zones of standard antibiotic ciprofloxacin as positive control and DMSO as negative control. The antifungal activity of newly synthesized compounds was tested against the two fungal strains, Aspergillus niger and Alternaria alternata by a agar well diffusion method reported earlier [27]. The fungal strains were maintained on peptone-dextrose agar slants at 30 °C. In this method, standard antifungal agent fluconazole was considered as positive control and DMSO as negative control. All the experiments were carried out in triplicate.

Result and discussion

The analytical data along with some physical properties of the ligand and its metal complexes are summarized in Table 1.

The elemental analysis of all complexes was analyzed by EDS/EDX spectrum and CHN analyzer. This shows the stoichiometry of complexes matched with percentage of C, H, N and O. The metal, chloride analysis was also done by EDS spectra. Some of the complexes were analyzed by EDS and CHN analyzer (supplementary figure S1).

Table 1	The physical prope	erties and analyt	tical data o	f the ligan	id and the	sir metal comp	lexes					
Sr. No.	Complexes	Color	Mol. Wt.	M.P °C	%Yield	EDX analysis c	calculated (four	nd)C, H, N, O an	alysis			Molar conduct-
						C	Н	0	z	CI	M	ance 22 ⁻¹ cm ²
L1	[C ₉ H ₇ NO]	White	145.15	74	I	74.47 (74.50)	4.86 (4.86)	11.02 (11.00)	9.65 (9.58)	1	1	1
L2	$[C_{12}H_9O_3CI]$	Yellow	208.59	162 °C	73.46	60.90 (60.84	3.83 (3.81)	9.55 (9.50)	I	14.98 (14.86)	I	I
1	[C ₂₄ H ₂₂ Cl ₄ NiO ₈]	Green	638.93	202 d*	68.12	45.12 (45.10)	3.47 (3.45)	20.03 (20.00)	I	22.03 (22.10)	9.19 (10.11)	88.30
7	$[C_{24}H_{18} Cl_4 CuO_6]$	Dark green	607.74	194d*	70.95	47.43 (47.10)	2.99 (3.02)	15.82 (15.80)	I	23.33 (24.01)	10.46 (11.11)	76.4
3	$[C_{24}H_{22}CI_4CoO_8]$	Brown	639.17	113 d*	64.48	45.10 (44.95)	3.47 (3.47)	20.03 (20.19)	I	22.19 (22.10)	9.22 (9.50)	56.10
4	$[\mathrm{C}_{24}\mathrm{H}_{22}\mathrm{Cl}_4\mathrm{MnO}_8]$	Chocolate brown	635.17	167 d*	69.52	45.38 (45.30)	3.49 (3.45)	20.15 (20.14)	I	22.33 (22.19)	8.65 99.05)	40.32
5.	$[\mathbf{C}_{21}\mathbf{H}_{15}\mathbf{C}\mathbf{I}_{2}\mathbf{NNiO_{4}}]$	Celery green	474.94	385 d*	69.23	53.11 (53.22)	3.18 (3.16)	13.47 (13.24)	2.95 (2.45)	14.93 (14.04)	12.36 (12.23)	80.21
9	$[C_{21}H_{15}Cl_2CuNO4]$	Hunter Green	479.80	193 d*	72.38	52.57 (51.07)	3.15 (3.56)	13.34 (13.64)	2.92 (2.71)	14.78 (13.48)	13.24 (12.89)	33.62
2	$[C_{21}H_{19}Cl_2C_0NO_6]$	Metallic Bronze	511.21	200 d*	56.60	49.34 (48.53)	3.75 (4.10)	18.78 (18.15)	2.74 (2.55)	13.87 (13.00)	11.53 (11.23)	74.75
æ	$[\mathrm{C}_{21}\mathrm{H}_{19}\mathrm{Cl}_{2}\mathrm{MnNO}_{6}]$	Brown	507.22	205 d*	64.78	49.73 (48.96)	3.78 (3.70)	18.93 (18.90)	2.76 (2.64)	13.17 (13.12)	10.83 (11.23)	87.61
d *= de	composition temper	ature, $L1 = Qui$	inolin-8-ol,	L2 = 6-ct	nloro-5,7,	dimethyl-4oxo	-4H-chrome	ne-3-carbaldeh	yde			

= 0-cnloro-3, /, dimetnyl-40x0-4H-cnromene-3-carbaldenyde = decomposition temperature, L1 = Quinolin-8-01, L2

Fourier transformer infrared spectra

In order to study the bonding mode of ligand to metal in the complex, FTIR spectrum of the free ligands L1 and L2 was compared with the spectra of their metal complexes.

The free ligand **L2** exhibits FTIR band at, $\nu_{C=0}$ (1718 cm⁻¹) belong to aldehyde group of pyrone ring [28]. The frequency 1656 cm⁻¹indicates $\nu_{C=0}$ belong to cyclic carbonyl group which are present to pyrone ring that is cyclic ketone [29]. The frequency 916–946 cm⁻¹ indicates enone system in resonance with aldehyde and conjugated double bond [30].

In the FTIR spectra of all the complex (1)–(8), the band of $\nu_{C=0}$ was shifted to lower frequency by some unites in all the complexes indicate bonding toward metal [31]. The another band of frequency 1656 cm⁻¹ was found to decrease by 2–56 cm⁻¹ unit toward 1600 cm⁻¹. That was attributed to donation of electron from $\nu_{C=0}$ group of cyclic ketone. The infrared of prepared complexes has shown bands of ν_{M-0} group in the infrared characteristics frequencies [32–34] are given in the Table 2.

In case of heteroleptic ligand complexes (5)–(8), the ν_{M-N} bond frequency is obtained due to the quinolin-8-ol bonded toward the metal though one of the nitrogen and second of the oxygen. The characteristic frequency of ν_{M-N} band obtained in between 635 cm⁻¹ and 825 cm⁻¹ depends on the metal complexes, while in complexes (1)–(4) lies in range 612–683 cm⁻¹ depends on the metal ions interact with ligands [35].

Electronic spectra and magnetic studies

The electronic spectra of ligand **L2** were shown the 26,246.72 cm⁻¹ and another band at 35,211.27 cm⁻¹ indicate $n-\pi^*$ and $\pi-\pi^*$ transition, respectively [29, 30]. The electronic spectrum (Supplementary figure S2) of the complex was measured at 26 °C in 10⁻³M concentration DMSO solvent. The electronic spectra for Ni(II) complexes (1) and (5) shows three bands at 21,091.26 cm⁻¹, 30,374.83 cm⁻¹ and 20,233.49 cm⁻¹, 32,412.81 cm⁻¹ and 47,619.05 cm⁻¹, respectively. The (5) shows band assignment is due to the ${}^{3}A_{2}g \rightarrow {}^{3}T_{2}g$, ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g$ and ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g$ (P) transitions. The complex (1) shows magnetic moment 2.92BM is indicate the complex (1) is paramagnetic in nature having octahedral geometry. While the complex (5) doesn't shows magnetic moment, it indicates that the complex (1) shows square planer geometry [36, 37].

The electronic spectral data of complex (2) showed in the range at 27,100.27 cm⁻¹ due to the ${}^{2}B_{1}g \rightarrow {}^{2}B_{2}g$ transition. While complex (6) shows 26,041.67 cm⁻¹ this band was attributed to the transition of electron from ${}^{2}B_{1}g \rightarrow Eg$ and the complex (6) display another bands at 32,258.06 cm⁻¹ corresponding to the intra-ligand transitions and an expected blue shift was observed compared with the ligand. This is compatible with this complex having square planer geometry. This is supported by magnetic moment values for complex (2) and (6) were 1.83 BM and 1.84 BM, respectively, this indicates that complexes have square planar geometry [38–41].

Sr.No.	Compound/Complexes	°H2O cm ⁻¹	^o C=O (Pyron) cm ⁻¹	^v C=N cm ⁻¹	$^{\mathrm{o}}\mathrm{C-O}~\mathrm{cm}^{-1}$	^v C=0 cm ⁻¹	$^{\mathrm{o}}\mathrm{M-N}~\mathrm{cm}^{-1}$	$^{\circ}M-O~cm^{-1}$
L1	$[C_9H_7NO]$	1	. 1	1425 cm^{-1}	1215 cm^{-1}	1	I	I
L2	$[C_{12}H_9O_3CI]$	I	$1656 \mathrm{cm^{-1}}$	I	$1310~{ m cm}^{-1}$	$1718 {\rm cm^{-1}}$	I	I
1	$[C_{24} H_{22} Cl_4 NiO_8]$	3371 cm^{-1}	$1654 \mathrm{~cm^{-1}}$	I	1335 cm^{-1}	1715 cm^{-1}	I	639 cm^{-1}
2	$[C_{24}H_{18} Cl_4 CuO_6]$	3461 cm^{-1}	1648 cm^{-1}	I	$1326 {\rm cm^{-1}}$	$1750 {\rm cm}^{-1}$	I	641 cm^{-1}
3	$[C_{24}H_{22}Cl_4CoO_8]$	$3335 \ {\rm cm^{-1}}$	$1616 {\rm cm^{-1}}$	I	1343 cm^{-1}	1742 cm^{-1}	I	612 cm^{-1}
4	$[C_{21}H_{15}Cl_2NNiO_4]$	$3253 \ {\rm cm^{-1}}$	$1600~{ m cm}^{-1}$	I	1399 cm^{-1}	1742 cm^{-1}	I	683 cm^{-1}
5.	$[C_{21}H_{15}Cl_2CuNO4]$	$3457~\mathrm{cm}^{-1}$	$1648~{ m cm}^{-1}$	1512 cm^{-1}	1367 cm^{-1}	1722 cm^{-1}	517 cm^{-1}	825 cm^{-1}
9	$[\mathbf{C}_{21}\mathbf{H}_{19}\mathbf{C1}_{2}\mathbf{C0}\mathbf{N0}_{6}]$	$3529~\mathrm{cm}^{-1}$	1648	$1503~\mathrm{cm}^{-1}$	$1458 {\rm cm^{-1}}$	1739 cm^{-1}	436 cm^{-1}	635 cm^{-1}
7	$[C_{21}H_{19}C1_2MnNO_6]$	$3502~\mathrm{cm^{-1}}$	1617 cm^{-1}	1539 cm^{-1}	$1467 \ {\rm cm^{-1}}$	1704 cm^{-1}	$508~{ m cm}^{-1}$	644 cm^{-1}
8	$[C_{21}H_{15}Cl_2NNiO_4]$	3384 cm^{-1}	1602 cm^{-1}	1476 cm^{-1}	$1458 \ {\rm cm^{-1}}$	1721 cm^{-1}	527 cm^{-1}	752 cm^{-1}

 Table 2
 FTIR frequencies of the bands of ligands and its complexes

The complex (3) and (7) is the complex of Co(II) metal ion. These complexes were found to have octahedral geometry. The electronic spectral band occurs at 27,244.99 cm⁻¹, 32,953.27 cm⁻¹ and 38,463.02 cm⁻¹, 13,605.44 cm⁻¹, 17,032.87 cm⁻¹ and 28,955.29 cm⁻¹. The band observed is assigned to the transition ${}^{4}T_{1g}$ (F) $\rightarrow {}^{4}T_{2g}$ (F), ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}$ (F) and ${}^{4}T_{1g}$ (F) $\rightarrow {}^{4}T_{2g}$ (P), respectively, it is suggesting that both the Co (II) complexes are octahedral geometry. The result of electronic spectra was supported by magnetic moment values for complex (3) and (7) were 4.92 BM and 5.05 BM, respectively [42–45].

The spectrum for complex (4) and (8) shows two bands at 29,585.80 cm⁻¹ and 34,843.21 cm⁻¹, respectively, which may be assigned to ${}^{6}A_{1}g \rightarrow {}^{4}Eg(G)$ and the ${}^{6}A_{1}g \rightarrow {}^{4}Eg(D)$ transition and is suggestive of octahedral geometry. The magnetic moment of Mn(II) complexes (4) and (8) measured on Gouy balance methods at room temperature. The value for complex (4) and (8) was found about 5.86 BM and 5.93 BM this result was supported to electronic spectrum and possible structures [46].

¹H spectra of ligand

The NMR spectra of the free ligand L2 have been recorded in DMSO-d₆. The ligand exhibits aromatic and aldehyde proton. The spectrum shows all proton signals was singlet. The signal for the aldehyde proton appeared at δ 10.32 ppm. The other signals are occurs at δ 8.4(S, 1H), 7.27(S, 1H), while the two methyl groups attached to the 3-formylchromenes moiety were appeared at δ 2.51(S 3H) and δ 2.99 (S, 3H) the



Fig. 1 NMR spectra of ligand (L2)

second methyl proton get deshielded due to resonance effect. The NMR spectrum is shown in Fig. 1.

Mass spectra of ligand

The mass spectra of the 6-chloro-5-7-dimethyl-40x0-4H-3-carbaldehyde chromone **L2** revealed the molecular ion peak at m/z 237 [M+H], which is match with the chemical formula weight (236.00) for the ligand and supports the formation of the compound. The LC–MS spectra of **L2** are shown in (Supplementary figure S3).

ESR spectra for complexes (2) and (6)

The room temperature ESR spectra of Cu(II) complexes (2) and (6) in solid state shows broad signal without hyperfine lines. They exhibit axial signal with g_{av} values 2.23 and 2.11, respectively, for the complexes (2) and (6) [47]. The g_{av} values are greater than free ion g value (2.0023), it indicates that the Cu(II) ions have axial symmetry with all the principal axes aligned parallel. Also, these higher g_{av} values of the complexes, indicating that complexes are partially covalent bond character in nature, and the ESR spectral values suggested that the complexes have square planar geometry [48].

The complex (2) and (6) have G-value were found to be 4.3466 and 4.1973, respectively. The G-values obtained for complex (2) and (6) are greater than 4, indicating the absence of exchange interaction between Cu(II) metal ions in the solid state. [49–51]. The ESR spectra of complexes are showed in Fig. 2.

Thermogravimetric analysis of complexes

In the present work, thermal analysis was carried out to obtain information about the thermal stability of the prepared complexes and decide whether the water or



Fig. 2 ESR spectra of copper complexes (2) a. and for (6) b complexes



Fig. 3 Thermogram of complexes a. (1)–(4) and b. (5)–(8)

solvent molecules are outside or inside the inner coordination sphere of the metal [52, 53]. The TG curves for all the metal complexes shown are in Fig. 3a complexes (1)–(4) and Fig. 3b complexes (5)–(8). The thermogravimetric analysis was done by non-isothermally with heating rate 10 °C/min up to the temperature 1000 °C. The sample undergoes some changes in air atmosphere. Metal complexes decompose continuously with evolution of gases and finally formation of respective metal oxides [54].

The TG curve of complex (1) shows that, decomposition occurs into two steps. In the first step, the chromone ligand (L2), water and chloride species were found to loss, the % weight loss was found to be 45.38%, which was attributed to theoretical % weight loss 46.19% in the temperature range 202–249 °C. The second decomposition step occurs in temperature range 429–471 °C, the % wt. loosened to be 23.30%, which matches with wt. loss 24.34% and was attributed to loss of quinolin-8-ol and formation of NiO residue.

The complex (2) is stable up to 190 °C. The first step show loss of 65.884% which is attributed with calculated % Wt. loss 67.68% and is equivalent to two molecules of $[C_8H_8ClO]$ and two CO from ligand in metal-ligand complex at 190–209 °C. In second step, the % Wt. loss was 9.632% was attributed with calculated % Wt. loss 10.28% indicate the loss of $2[C_3H_4O]$ molecules at 288.19–329.45 °C. The final decomposition product was CuO residue. The CuO residue stable up to the 1000 °C shown in Fig. 3. complex (2).

The TG curve of Co(II) complex (3) was carried out in N₂ atmosphere. The complex shows two decomposition steps. The first step is accompanied by mass loss 20.43% and the second step 73.23% at temperature 113-124 °C and 307–665 °C, respectively. In the step-I, the loss of coordinated water, chloride ions, is corresponding to theoretical mass loss (19.43%). And last step was breaking of the chromones ligand, which was also match with theoretical mass loss 74.87%. The final product obtained in this complex was CoO.

The result of complex (4) shows a good agreement with the theoretical formula as suggested from the analytical data. This complex decomposes in three steps. In the first step, estimated wt. loss 3.798% (calculated mass loss 5.60%) may be attributed to the loss of two coordinated water molecules in the temperature range 167.00-200 °C. The second step is in the temperature range 236.77-415.88 °C, with an estimated mass loss 82.021% (calculated mass loss 84.80%). This was corresponding to the loss of organic chromone ligand present in the complex. The final step was horizontal plateau was observed in the temperature greater than 586 °C with estimated mass loss 15-13% for the formation of black residue of MnO₂.

The complex (5) decomposes in one step process. The procedural decomposition temperature was started at 385 °C and end with 396 °C. The theoretical percent weight loss 81.56%. This was attributed to the loss of quinolin-8-ol and chromone moiety. The practically Wt. loss is 82.49%. The remaining residue was found to be of NiO.

The Cu(II) complex (**6**) undergoes two step decomposition. The % wt. loss in first step was found to be 28.57%, and theoretically it was 28.43% in at temperature range 193–275 °C. This was attributed to loss of quinolin-8-ol ligand and further decomposition occurs continuously up to the temperature 553 °C. In this the wt. loss, it was found to be 64.65% is match with 65.01%. This result was attributed to loss of chromone ligand and formation of chocolate brown powder of copper oxide [55].

The complex (7) decomposes in only one step. The decomposition starts at temperature 200 °C and stop at the temperature 604 °C. Theoretically, the % wt. loss was 89.66% due to loss of both the ligands and two coordinated water molecules. The practically % wt. loss was found to be 91.095%. The complex get decomposed and formation of cobalt oxides residue [56].

The Mn(II) complex (8) is thermally stable up to the temperature 202 °C. The first decomposition step was started by percentage wt. loss 27.13, which is attributed to % wt. loss 26.76 corresponding to loss of N, O-donor ligand. Then, further the thermogram was continuous up to the temperature 551.74 °C by loss of remaining organic part of the complex. The % wt. loss was 68.87% which was match with the calculated wt. loss 69.87%. The formation of final product was MnO₂ residue.

Table 3 Powder	X-ray diffraction p	attern for complexe.	s (1)–(8)					
Complex	(1) $[C_{24}H_{22}Cl_4NiO_8]$	(2) $[C_{24}H_{18}Cl_4NiO_6]$	(3) $[C_{24}H_{22}Cl_4CoO_8]$	(4) $[C_{24}H_{22}Cl_4MnO_8]$	$(5) \\ [C_{21}H_{15}Cl_2NNiO_4]$	$ (6) [C_{21}H_{15}Cl_2NNiO_4] $	$\begin{array}{c} (7) \\ [C_{2l}H_{15}Cl_2NNiO_4] \end{array}$	$ [C_{2_1}H_{1_5}Cl_2NNiO_4] $
JCPDS No.	43-1973	42-1925	45-1708	83-2179	13-0739	42-1745	25-1625	46-1871
Formula weight	638.93	607.74	639.17	635.17	505.98	510.83	542.25	538.25
Crystal color	Green	Dark green	Brown	Chocolate brown	Celery green	Hunter green	Metallic bronze	Brown
Temperature(K)	298	298	298	298	298	298	298	298
Wavelength (Å)	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.54
Radiation	$CuK\alpha$	$CuK\alpha$	CuKa	$CuK\alpha$	$CuK\alpha$	CuKα	$CuK\alpha$	$CuK\alpha$
Crystal system	Monoclinic (P)	Tetragonal	Monoclinic (P)	Orthorhombic(P)	Monoclinic (P)	Monoclinic (P)	Monoclinic (P)	Tetragonal
Space group	P2 ₁ /c(14)	P2 ₁ /c(14)	P2 ₁ /c(14)	Pbnm(62)	1	P2 ₁ /c(14)	P2 ₁ /c(14)	1
A	0.7806	I	0.5948	1.3060	2.0561	0.7806	1.1204	I
C	1.2891	1.0465	0.9911	1.2870	2.0935	1.2891	1.4263	0.8847
Z	I	I	2	4	I	4	2	I
a (Å)	11.88(3)	9.448	7.4725(7)	12.45	11.00	6.978(1)	7.91(7)	15.18
b (Å)	15.22(4)	18.646	12.5635(14)	9.534	5.35	12.71(2)	7.06(14)	15.18
<i>c</i> (Å)	19.623(6)	9.018	12.4516(14)	12.27	11.230	23.10(5)	10.07	13.43
α (°)	06	06	90.00	06	06	06	90.00	06
β (°)	06	113.62	102.80(9)	90	106	97	101.3	06
γ (°)	06	06	90.00	90	90	06	90.00	06
alb	0.7757	0.5067	0.9911	0.9855	2.0935	1.8166	1.4263	0.9855
clb	0.6056	0.4836	0.5948	0.7657	2.0561	0.5488	1.1204	0.7657
Volume	3549.47	1455.62	1139.90	1456	1455.62	2034.44	551.45	1456

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Powder X-ray diffraction study

The powder XRD pattern (Supplementary figure S4) of all the homoleptic and heteroleptic complexes was recorded over the $2\theta = 20-80^{\circ}$ range [57, 58]. The all metal complexes exhibit crystalline nature. This XRD study also one of the evidence about formation of metal-ligand complexes. The XRD unit cell parameter such as crystal nature, bravis lattices, diffraction angles, cell length and volume is illustrated in Table 3. The complexes (1) to (4) shows sharp peak (Fig. 5) as compared with the heteroleptic ligand complexes (5)–(8). The heteroleptic ligand complexes shows broad peak indicating the formation of nanocrystalline nature of the complexes.

Scanning electron microscopy

The external surface structure of all the complexes has been illustrated by scanning electron microscopy.

The SEM micrographs of all eight complexes are shown in Fig. 4 The complex (1)-(4) shows flower, foil, mushroom and ice-stone like morphology, respectively [59, 60]. While its heteroleptic metal complexes of chromones derivatives changes the morphology in case of complex (5)-(8). The micrograph of complexes shows spherical ball shape, sheet like, rock and the rough rock-type morphology. The grain size of heteroleptic ligand metal complexes (5)-(6) was determined from Scherer's equation [54]. This was found 5.03 nm, 4.43 nm, 5.4254 and 42.31 nm, respectively. It was clearly indicate that formation of nanocrystalline complexes [61, 62].

Molar conductance

The molar conductance of the complexes is measured in DMSO because of the all complexes are soluble in it. The concentrations 10^{-3} M of all complexes were made at 25 °C. The observed conductance values are moderate for the all complexes, it indicate that the complexes were electrolytic in nature (Table 1).

Antimicrobial activity

The antibacterial activity of newly synthesized compounds was tested against the two bacterial strains, *S. typhi* and *B. subtilis*. A representative Fig. 5 and Table 4 show maximum zone of growth inhibition of **L1** on nutrient agar plates. This indicates that **L1** has highest antibacterial activity against both gram-positive and gramnegative bacteria when compared with its zone of inhibition with other compounds. In contrary, **L2** complex (2), (3), (4), (6) and (7) have moderate antibacterial activity when compared with control. Similar antibacterial activity of silver and gold nanomaterials is reported earlier [63]. It was also seen that complex 5 and 8 did not showed any antibacterial activity. Thus, the study revealed that variation in antibacterial activity might be due to varying in size and chemical nature of compounds. Similarly, antifungal activity of these compounds was tested against two fungi, *A. niger* and *A. alternata* as shown in Table 4. The order of compounds for its antifungal





Fig.4 SEM images of the all (1–8) complexes with morphography. (I) For complex(1)–(4) in the scale of (a) The left hand side picture is 10 μ m scale, (b) The middle picture is 5 μ m and (c) The right hand side picture is 1 μ m in scale. (II) For complex(5)–(8) in the scale of (e) The left hand side picture is 5 μ m scale, (f) The middle picture is 2 μ m and (g) The right hand side picture is 1 μ m in scale



Fig. 5 A representative images of antimicrobial activity of L1 with (a) control [without L1] (b) *S. typhi*; (c) Antifungal activity of complex (5) against *A. Altenaria* (d, e) Antibacterial activity of complex (6) &(7) against *S. typhi* (f) Antifungal activity of complex (8) against A. *Altenaria*

Complex/compound	Diameter of zon	e of inhibition (mm))	
	B. Substilis	S. Typhi	A. niger	A. alternata
L1	32 ± 0.81	30 ± 0.75	35 ± 0.91	35 ± 0.91
L2	15 ± 0.25	13 ± 0.21	30 ± 0.80	30 ± 0.75
(1)	00	00	15 ± 0.20	18 ± 0.20
(2)	15 ± 0.15	14 ± 0.18	18 ± 0.21	25 ± 0.25
(3)	16 ± 0.16	16 ± 0.15	22 ± 0.25	22 ± 0.25
(4)	15 ± 0.15	12 ± 0.10	27 ± 0.75	30 ± 0.84
(5)	00	00	30 ± 0.72	28 ± 0.65
(6)	18 ± 0.16	15 ± 0.15	37 ± 0.82	30 ± 0.84
(7)	20 ± 0.17	16 ± 0.18	32 ± 0.81	24 ± 0.15
(8)	00	00	30 ± 0.81	28 ± 0.81
Ciprofloxacin	40 ± 0.93	35 ± 0.71	-	-
Fluconazole	-	-	42 ± 0.95	36 ± 0.61

 Table 4
 Antimicrobial activity of ligands and metal complexes

activity against *A. niger* was observed as follow: complex (6) > L1 > (7) > L2, complex (5), (8) > (4) > (3) > (2) > complex (1). Thus, it was seen that complex (6) shows maximum antifungal activity against the fungus, *A. niger*. The order of compounds for its antifungal activity against *A. alternata* was observed as follow: L1 > L2, complex (4 and 6) > complex (3 and 8) > (2) > (7) > (3) > complex (1). Thus, study revealed that L1 shows highest antifungal activity against the fungus, *A. alternata* as

shown in Table 4. Similar antifungal activity was also seen with metal nanomaterials reported earlier [64, 65].

Structure-activity relationship

Several structures of flavonoids were identified which possessing antifungal, antiviral and antibacterial activity reported earlier. Many high-quality investigations carried out to understand the relationship between flavonoid structure and antibacterial activity. These investigations are in close agreement. Several flavonoid compounds showed inhibition of DNA gyrase enzyme. Many other flavonoid compounds revealed inhibition of cytoplasmic membrane function and energy metabolism. The lipophilic nature of these compounds may cause rupture of cell membrane, resulting in a collapse of vital cell functions and, consequently the cell death [66, 67]. Flavonoid-metal ions complexes penetrate more easily through cell wall due to its protein denaturation potential [68]. The 8-hydroxyquinon compound showed efficient antimicrobial activity against the gram-positive bacteria and diploid fungi reported earlier. The compound has lower lipophilic in nature get easily adsorb on the bacterial cell wall contain hydrophilic polysaccharides and charged amino acids in their peptidoglycan [69]. The electron microscopic study also revealed that quinolin-8-ol compound disrupt the bacterial cell walls which caused the cell lysis and cell death [70]. The quinolin-8-ol has metal chelating property, they form different metal complexes [71]. These metal complexes have similar structures and geometries. Thus, complex formation with such metals modulates the antimicrobial activity reported earlier [72, 73].

Conclusion

The heteroleptic ligand transition metal complex of 6-chloro-5-7-dimethyl-4oxo-4H-chromene-3-carbaldehydes and quinolin-8-ol with Mn(II), Co (II), Ni (II) and Cu (II) metal ions found to be new and unreported. All the complexes were characterized by on spectral, thermal, X-ray diffraction and a number of microanalytical techniques. The composition of complexes was analyzed by C, H, O elemental analysis and EDS. It was found to be calculated % of atoms match with experimental analysis. The FTIR shows the carbonyl oxygen of Pyron and aldehyde carbonyl oxygen donate the electron to the metal and form metal-ligand complex as well as the formation of heteroleptic ligand complexes. The electronic spectra and magnetic susceptibility were suggested that the geometry and magnetic moment of particular complexes depend upon metal ions. The thermogravimetric studies indicate that the decomposition the complex and the final product were the metal oxide of corresponding to those metal complexes.

The powder XRD shows the complexes were nanocrystalline in nature. The XRD result was supported by the SEM micrograph. All the complexes were electrolytic in nature. The antimicrobial activity against *S.Typhi* shown by both the ligands. The Ni(II) does not show antibacterial activity, while complexes Cu(II), Co(II) and

Mn(II) shows good activity against the gram-positive and the gram-negative bacteria. The heteroleptic ligand complex (6) of Cu(II) shows higher antifungal activity as compared with Ni(II), Co(II) and Mn(II) complexes.

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