
Research Article

Theme- New horizons in chemical sciences.

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Synthesis, spectral study, characterization of cobalt (II) and copper (II) complexes of chalcones.

S. N. Ipper*¹, N. K. Raut², P. P. Dixit³, G. K. Kakade⁴

¹Department of Chemistry, Sunderrao Solanke Mahavidyalaya, Majalgaon, Beed, Maharashtra, India.

²Department of Physics, Sunderrao Solanke Mahavidyalaya, Majalgaon, Beed, Maharashtra, India.

³Department of Microbiology, Dr. B. A. M. U. Sub-campus, Osmanabad, Maharashtra, India.

⁴Department of Chemistry, A. C. S. College, Kille-Dharur, Beed, Maharashtra, India.

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***Corresponding author E-mail address: isn13@rediffmail.com**

ABSTRACT

Metal complexes of Co(II) and Cu(II) have been synthesized with newly prepared biologically active ligands. These ligands were prepared by the Claisen-Schmidt condensation method of 2,6-dihydroxy acetophenone and 5-methyl-2-furaldehyde. The structures of the complexes have been proposed by the analytical data, conductivity measurement, magnetic moment, IR spectrum, Electron absorption spectrum, thermal studies, and XRD analysis. Analytical data confirmed 1:2 stoichiometry and the electronic spectral data, IR, magnetic moment, TG-DTA suggests that Co(II) and Cu(II) complexes have octahedral geometry. The presence of coordinated water molecules in Co(II) and Cu(II) complexes is confirmed by TG-DTA studies. The conductivity data show that all these complexes are non-electrolytes. Antimicrobial activities of complexes with selected bacterial strain and fungal strain carried out and the results have been compared with commercial standards. In this paper, we prepare chalcone of 5-methyl furfural by Claisen-Schmidt condensation method and synthesize Co(II) and Cu(II) metal complexes and characterize them by Infra-red, Electronic absorption spectra, magnetic susceptibility, CHO analysis, solution conductivity, XRD study, TG-DTA, and antimicrobial activity.

KEYWORDS

Transition metal complex, Electron absorption spectrum, Infrared spectrum, TG-DTA.

1. INTRODUCTION

Chalcones constitute an important group of natural products, chemically they consist of open chain flavonoids in which the two aromatic rings are joined by α , β unsaturated carbonyl system. The name chalcone is given by Kostanecki and Tambar[1]. Cobalt(II) and Copper(II) complexes of chalcones are synthesized and studied in the literature [2-3]. It is believed that the ($>CO-C=C<$), moiety imparts biological characteristics to this class of compounds. Such α,β -unsaturated carbonyl compounds, and their metal complexes possess interesting biochemical properties, such as antitumor, antioxidant, anti-fungal and antimicrobial activities[4]. The electronic absorption spectrums, infrared spectrum, magnetic moment, TG-DTA support the octahedral geometry of the metal complexes of chalcones. All crystals of a substance possess the same elements of symmetry. The atoms in the plane are responsible for the scattering of X-rays. The spacing d depends on the dimensions of the unit cell. The relative intensities of orthorhombic, monoclinic, and triclinic are characterized by 3, 4 or 6 lattice constants. The powder XRD method is used in the present investigation for crystal structure determination. It gives information about inter atomic distance[5]. The pykometric densities of each of the complexes were determined using a specific gravity bottle by the principle of Archimedes[6]. Depending on these values of axial length and axial angles the crystal is classified as cubic, tetragonal, orthorhombic, trigonal, hexagonal, monoclinic and triclinic structures. The computer program, used for indexing data was powder-X. In this program all the essential features of X-ray program are presented and in addition it calculates the deviation in lattice parameter a , b , c in Å and α , β and γ in degree and minutes with better combination of h , k , l values until the final deviation is within the permissible limit of 2%. The refined values also give the volume of the unit cell. By using the literature value for a definite crystal system, the probable space group was assigned to each of the complexes. Furthermore, biological activities of complexes with selected bacterial strain and fungal strain carried out and the results have been compared with the commercial standard[7]. The X-ray powder diffractogram of the metal complexes was used for the structural characterization and determination of lattice dimensions. In this paper, we prepare chalcone of 5-methyl furfural by Claisen-Schmidt condensation method and synthesize Co(II) and Cu(II) metal complexes and characterize them by Infra-red, Electronic absorption spectra, magnetic susceptibility, CHO analysis, solution conductivity, XRD study, TG-DTA, and antimicrobial activity.

2. MATERIALS AND METHODS

2.1. Synthesis of chalcone of 5-methyl furfural

The reagents used for the preparation of furan chalcone are of A.R. grade. The mixture of 2,6, dihydroxy acetophenone (0.01 mol) and 5-methyl-furaldehyde (0.01 mol) are dissolved in ethanol (20ml) and then sodium hydroxide 10ml (40%) was added to it. The mixture was stirred for 3 hours till brown colored precipitate was observed. The progress of the reaction was monitored by TLC. After completion of the reaction, the contents were poured into ice water and

then acidified by dil. HCl. The solid obtained was filtered and the crude product was recrystallized from ethanol to give the chalcone [8-9].

2.2. Synthesis of metal complex

The solution of 0.02 mole of chalcone of 5-methyl furfural was taken in a round bottom flask containing 30 ml of anhydrous methanolic solution of chalcone of 5-methyl furfural was used and boiled for 10 minutes. A hot solution of 0.01 mole, of Cu(II) sulfate and Co(II) nitrates in 20 ml of methanol was added drop wise to the solution of the chalcone of 5-methyl furfural. To this reaction mixture, 10% alcoholic ammonia was added up to slightly alkaline pH. The complexes of different metals were precipitated at different pH range. The pH8-10 range was definite for these complexes.

The contents were stirred on a magnetic stirrer for one hour. The solid metal complex separated and washed with methanol three to four times. Dried in vacuum desiccators over anhydrous granular calcium chloride. The melting point/decomposition temperatures of the complexes were determined by Thiele's melting apparatus. The reactions of the formation of Co(II) and Cu(II) complexes are shown in figure (1). The IR spectrum was measured at CIL, Chandigarh, Punjab, Electron absorption spectrum at Sunderrao Solanke Mahavidyalaya Majalgaon and CHO analysis, TG-DTA and XRD measured at SAIF Cochin, Kerala.

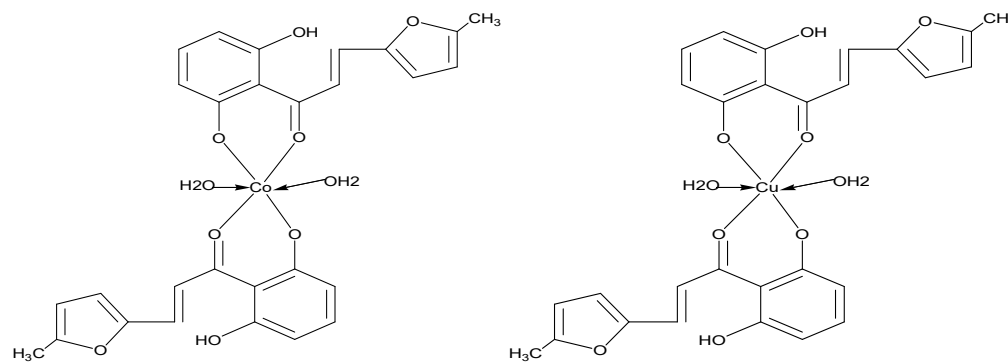


Fig.1. Metal complexes of cobalt (II) and copper (II) with chalcone of 5-methyl furfuraldehyde.

3. RESULTS AND DISCUSSION

3.1. Infra-red spectrum

The infrared spectrum of Co(II) complex

The infrared spectra of ligands and Co(II) complex of chalcone of 5-methyl furfural were recorded on a Perkin-Elmer Spectrum RX-IFTIR Spectrophotometer over the range 4000-400 cm⁻¹ using KBr pellet at CIL, Chandigarh, Punjab. The number in the spectrum of the complex indicates coordination through the oxygen of (C=O) group. The M-O bond for Co(II) complex is observed at 510-600cm⁻¹[10]. The presence of phenolic -OH is confirmed by peaks at 3420cm⁻¹ and 3037 cm⁻¹ in the ligand, In the spectrum of Co(II) complex, there is complete disappearance of peaks at 3420cm⁻¹ and 3037 cm⁻¹ in chalcone suggesting absence of phenolic group -OH indicates its co-ordination,(C-O-C) is shifted to a lower wave number comparing with free ligand. In the IR spectrum of Co(II) complex, the strong bands that appeared in the region 1623

cm⁻¹ are assigned to ν (C=O) of stretching frequency. It is shifted towards lower frequency than the corresponding ligand and appeared at 1590 and 1611 cm⁻¹ in metal complexes. Such a lowering in stretching vibration of ν (C=O) in chalcone indicates the participation of chalcone carbonyl in complexation. In the IR spectrum of Co(II) complex: the new bands are observed at 3263 cm⁻¹ and 3162 cm⁻¹ which are due to the -OH intense broadband of co-ordinate water molecules. In Co(II) complex new band is observed at 510-600 cm⁻¹ due to the (M-O) bond. The IR spectrum of Cu(II) complex of chalcone of 5-methyl furfural is presented in figure (1) and their group absorption frequencies are given in Table 1.

Chiara Sulpizio assigned that, IR spectra of Cu²⁺, the intensity of -OH vibration at 3300 cm⁻¹ reduced or broadened for copper complexes indicating that hydroxyl group would be interacting with metal. There is a shift of the carbonyl stretch from 1640 to 1610 cm⁻¹ for ligands in the presence of copper meaning that the bond strength of the C=O bond is weakened this is a strong indication for the participation of the carbonyl moiety in complexation process. Additionally, a new bond is observed at 500 cm⁻¹ in the spectra of metal complexes[11].

The presence of phenolic-OH in chalcone of 5-methyl furfural is confirmed by peaks at 3420cm⁻¹ in the ligand. In the spectrum of Cu(II) complex, the appearance of a peak at 3223cm⁻¹ in chalcone suggests the absence of phenolic group -OH indicates its co-ordination,(C-O-C) is shifted to a lower wave number comparing with free ligand [12]. In the IR spectrum of ligand, the strong band appeared in the region 1623 cm⁻¹ is assigned to ν C=O) of stretching frequency. It is shifted towards lower frequency than corresponding ligands and appeared at 1613cm⁻¹ in metal complexes. Such a lowering in stretching vibration of ν (C=O) in chalcone indicates the participation of chalcone carbonyl in complexation. In Cu(II) a complex new band is observed at 480 cm⁻¹ due to the (M-O) bond.

Table 1. Infrared absorption frequencies (cm⁻¹) of chalcone of 5-methyl furfural Co(II) and Cu(II) complexes.

Ligand/ Metal complexes	ν (OH) cm ⁻¹	ν (H ₂ O) cm ⁻¹	ν ((-CO- CH=CH-)cm ⁻¹	ν ((C- O-C) cm ⁻¹	ν (C=C) cm ⁻¹	Aromatic ring (C=C)cm ⁻¹ 1	ν (M- O)cm ⁻¹
chalcone of 5-methyl furfural	3420	-	1623	1095	1558	1439	-
[Co(chalcone of 5-methyl furfural) ₂]	3003	3263	1590	1024	1383	1220	580
[Cu(chalcone of 5-methyl furfural) ₂]	3223	3223	1613	1024	1582	1435	480

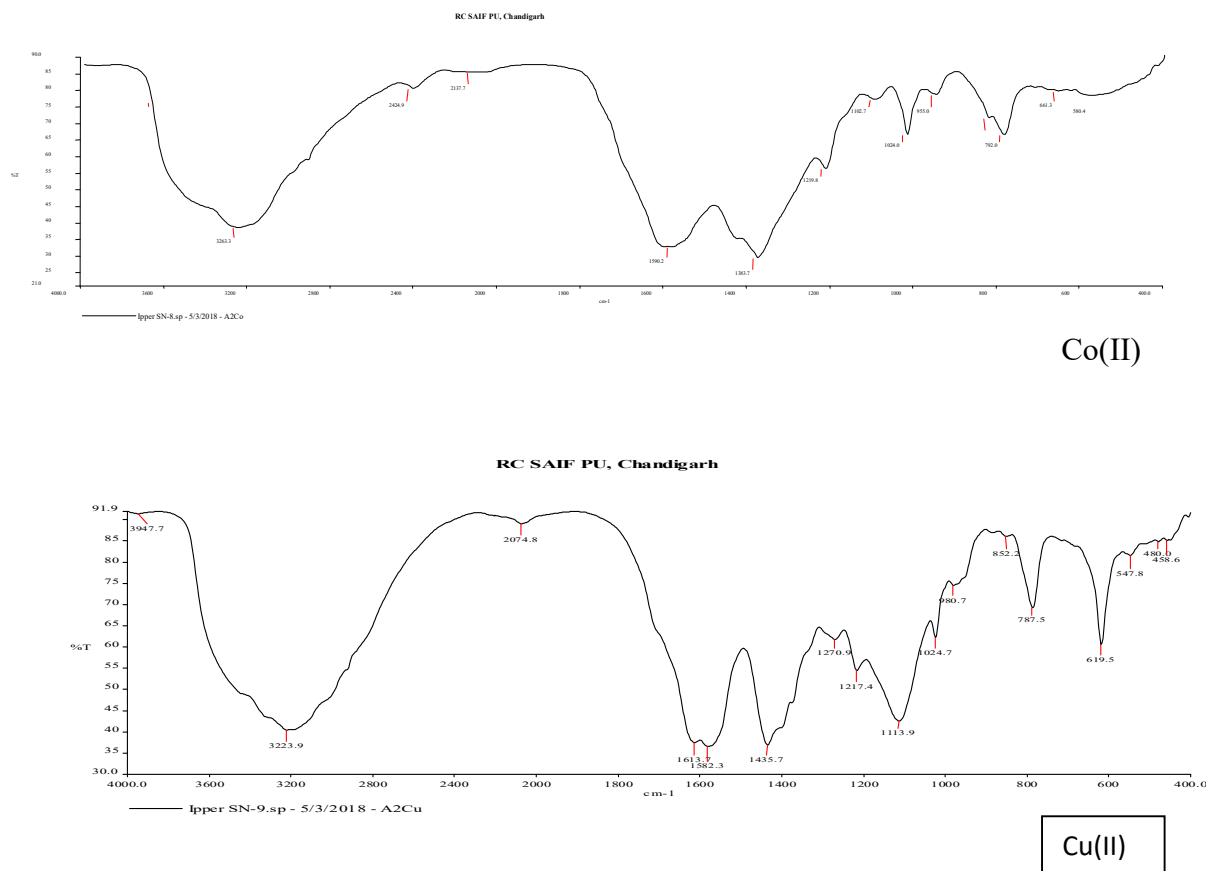


Fig. 2. Infrared spectra of Co(II) and Cu(II) metal complexes.

Table 2. Physical parameters of Cobalt (II) and Copper (II) complexes.

Metal complex	Ligand	p^H range ppt.	Color	M.P.^oC
cobalt(II) complex	chalcone of 5-methyl furfural	7.5 -8.5	coffee	>300
copper(II) complex	chalcone of 5-methyl furfural	7.0 - 7.5	brown	>300

CHO analysis

The carbon, hydrogen, oxygen, cobalt and copper metals percentage in Co(II) and Cu(II) complexes of chalcone measured at SAIF Cochin, Kerala. The calculated and measured values of CHO analysis are matching and are given in table no.(3).

Table 3. CHO analysis data.

Metal complexes	Chemical formula	Mol. Wt.	Elemental analysis:% found (calculated)						
			C	H	N	O	S	X(Br)	M
Co (II) complex	[C ₂₈ H ₂₆ O ₆ Co]	517	64.89 (64.99)	5.04 (5.06)	-	18.59 (18.55)	-	-	11.29 (11.39)
Cu (II) complex	[C ₂₈ H ₂₆ O ₆ Cu]	522	64.38 (64.42)	4.98 (5.01)	-	18.29 (18.38)	-	-	11.99 (12.17)

3.2. Magnetic susceptibility, solution conductivity, and electronic absorption spectral data
Magnetic susceptibility

The μ_{eff} (B.M.) values at room temperature for Co(II) complex is 4.57 B.M. and Cu(II) 1.85 B.M., these values agree with octahedral geometry of the metal complexes [13-14].

3.2.1. Solution conductivity

The solution conductivities of 10^{-3} M solution of the metal complex in DMSO were measured on Equiptronics digital conductivity meter EQ - 660 with $20 \mu\Omega$ to $200 \mu\Omega$ at 298K temperature. In the present investigation Co(II) and Cu(II) complexes are coffee and brown, stable to air and moisture. Decomposes at high temperatures rather than showing sharp melting points. They are insoluble in water and soluble in DMSO, DMF. The low conductivity values in the DMSO solution (10^{-3} M) are given in Table 4 indicates non-electrolytic nature.

3.2.2. Electronic absorption spectral study

The electronic absorption spectrum was measured on SL159, single beam UV-VIS spectrophotometer.

The electronic spectrum of Co(II) complex studied in the present investigation exhibit absorption bands at $25641(390 \text{ nm})\text{cm}^{-1}$ and $29411(340 \text{ nm})\text{cm}^{-1}$ which are assigned to ${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$ and charge transfer bands respectively.



Fig. 3. Electronic absorption spectra of Co (II) complex of chalcone of 5-methyl furfural.

Table 4. Solution conductivity, magnetic and electronic absorption spectral data of Co(II) and Cu(II) complexes.

Ligand	Metal complex	Molar Conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	μ_{eff} (BM.)	Absorption maxima cm^{-1} (nm)	
				${}^4\text{T}_{1g(\text{F})} \rightarrow {}^4\text{T}_{1g(\text{P})}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	Charge transfer
chalcone of 5-methyl furfural	Co(II) complex	4.37	4.57	25641(390)	29411(340)
chalcone of 5-methyl furfural	Cu(II) complex	3.0	1.85	25906(386)	34246 (292)

3.2.3. Thermal analysis Co(II) complex chalcone of 5-methyl furfural

The simultaneous thermogravimetric, differential thermal analysis of Co(II) complex chalcone of 5-methyl furfural was performed in an inert nitrogen atmosphere on Perkin Elmer STA 6000 at SAIF, Cochin, Kerala. The heating rate was $10^\circ/\text{min}$ and the flow rate of nitrogen 50 ml/min. The reference substance used was $\alpha \text{Al}_2\text{O}_3$ in a platinum crucible and the sample weighed in the range of 4-12 mg. The thermogram of Co(II) complex of chalcone of 5-methyl furfural is presented in figure (3). This curve reveals that there is a presence of lattice as well as coordinated water in the complex.

The TG curve of Co(II) complex of chalcone of 5-methyl furfural(Fig.4) shows first weight loss at 73.54°C indicating the presence of lattice water with weight loss 5.54% (calc. wt. loss 6.02%). The second loss due to a coordinated water molecule in the complex takes place at 150°C . In the third step loss of non-coordinated two fragments of 5-methyl-furan part of ligand takes place. In the fourth step weight loss of 31.74% (calc. wt. loss 31.03%) within the temperature range $300\text{-}350^\circ\text{C}$. which is authenticated by broad endotherm in the DTA curve at 319.29°C . The last stage decomposition occurs with a mass loss of 24.66% (calc. wt. loss 24.13%) in the range $360\text{-}510^\circ\text{C}$, due to the loss of two enone part of chalcones fragment. This is authenticated by broad endotherm in the DTA curve. Above 550°C , the TG curve attains a constant level corresponding to its metal oxide (CoO).

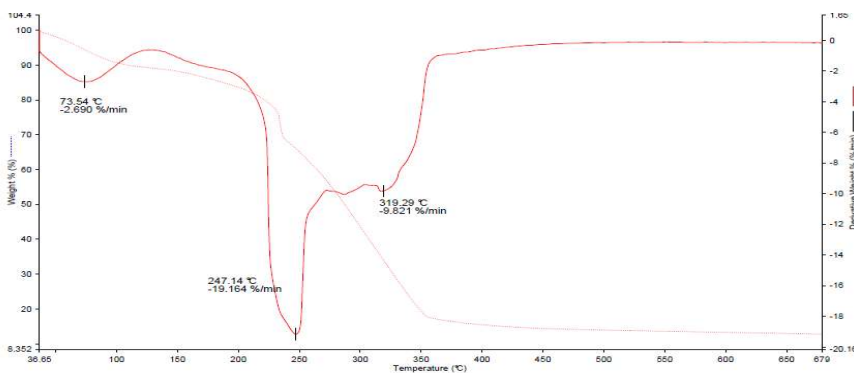


Fig. 4. TG-DTA curve of Co(II) complex of chalcone of 5-methyl furfural.

3.2.4. X-ray diffraction spectral studies of metal complexes

Cobalt (II) complex

The XRD spectral study has been done at SAIF, Cochin, Kerala. The X-ray diffraction patterns of Co(II) complex is shown in (Fig. 4). The standard deviation observed is within the permissible range. The observed and calculated densities of Co(II) complex of chalcone of 5-methyl furfural are 1.909 g cm^{-3} and 1.816 g cm^{-3} respectively. Chalcone of 5-methyl furfural of Co(II) complex is found to be monoclinic lattice type with space group P2/m and lattice parameters are $a=8.9169 \text{ \AA}$, $b=7.6183 \text{ \AA}$, $c=5.4089 \text{ \AA}$, $\alpha=90^\circ$, $\beta=98^\circ$, $\gamma=90^\circ$ satisfies the condition $\alpha=\gamma=90^\circ$, $\beta\neq90^\circ$ unit cell volume $V=231.24 \text{ \AA}^3$.

Copper (II) complex

The Cu(II) complex of chalcone of 5-methyl furfural was studied by X-ray powder diffraction (Fig.6). The standard deviation observed was within the permissible range. The observed and calculated densities are 1.7795 g cm^{-3} and 1.9753 g cm^{-3} respectively. The Cu(II) complex of chalcone of 5-methyl furfural is triclinic lattice-type P. For this complex lattice parameters are $a=11.23 \text{ \AA}$, $b=13.12 \text{ \AA}$, $c=17.00 \text{ \AA}$, $\alpha=85^\circ$, $\beta=81^\circ$, $\gamma=82^\circ$, $V=753 \text{ \AA}^3$. These values match with the study of Cu(II) complexes of chalcone derivatives were synthesized by Salima Tabti and et al.[15]. The values of unit cell data and crystal lattice parameters for Co(II) and Cu(II) complexes calculated from indexed X-ray diffraction data are as given below.

Unit cell data and crystal lattice parameters for Co(II)

$a (\text{ \AA}) = 8.9169, b (\text{ \AA}) = 7.6183, c (\text{ \AA}) = 5.4089, \alpha = 90^\circ, \beta = 98^\circ, \gamma = 90^\circ$, Standard deviation (%) = 0.18, Volume (V) = 231.24 \AA^3 , Density (obs.) = 1.909 g cm^{-3} , Density (cal.) = 1.816 g cm^{-3} , Z = 1, Crystal system= Monoclinic and Space group = P2/m.

Cu(II)

$a (\text{ \AA}) = 11.23, b (\text{ \AA}) = 13.12, c (\text{ \AA}) = 17.0, \alpha = 85^\circ, \beta = 81^\circ, \gamma = 82^\circ$, Standard deviation (%) = 0.17, Volume (V) = 753.05 \AA^3 , Density (obs.) = 1.7795 g cm^{-3} , Density (cal.) = 1.9753 g cm^{-3} , Z = 2, Crystal system= triclinic and Space group = P2/m.

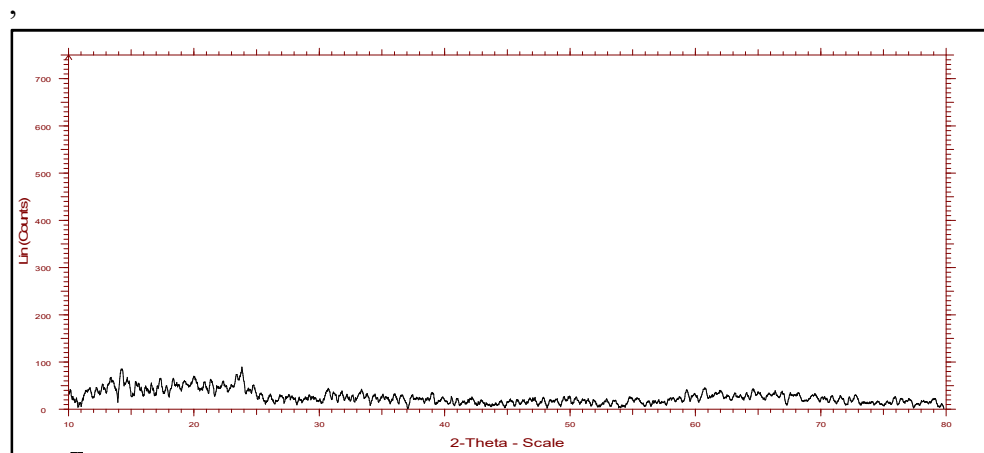


Fig. 5. X-ray diffractogram of Co(II) complex of chalcone of 5-methyl furfural.

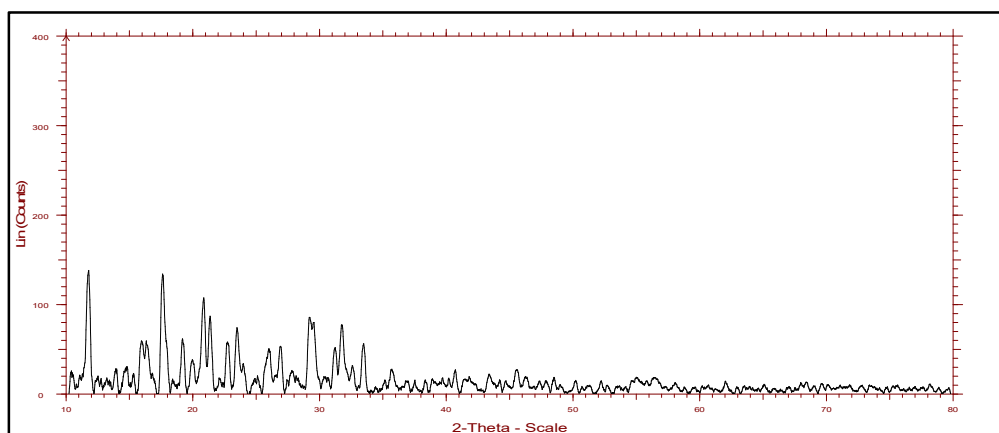


Fig. 6. X-ray diffractogram of Cu(II) complex of chalcone of 5-methyl furfural.

3.3. Antimicrobial activity

Antimicrobial activity was assayed by the cup plate agar diffusion method [15] by measuring inhibition zones in mm. In vitro antimicrobial activity of all synthesized compounds and standards have been evaluated against strains of bacteria *Bacillus cereus*, *Staphylococcus aureus* and strains of fungi *Aspergillus niger*, *Candida albicans* the standard used was penicillin and Griseofulvin. From the results of antimicrobial activity of ligands and complexes it is clear that the complexes show enhanced activity than ligands. The increase in antimicrobial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to the combined activity of the metal and ligands.

4. CONCLUSION

The Co(II) and Cu(II) complexes are colored, insoluble in most of the organic solvent but soluble in an organic solvent. The stoichiometry ratio of the metal complexes obtained is 1:2. The solution conductivity of these metal complexes reveals a non-electrolytic nature. The infrared spectral data indicate that the ligand act as mono negative bidentate species towards Co(II) and Cu(II) complexes. The electronic spectral data, IR spectrum, magnetic moment, TG-DTA suggests that Co(II) and Cu(II) has octahedral geometry. The CHO analysis gives C, H, and O percentages in the metal complexes. The XRD parameters show that the structure of Co(II) is monoclinic with space group = P2/m and that of Cu(II) is triclinic and has space group = P2/m.

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6. REFERENCES

1. Kostanecki, S.V. (1899). *J.Chem.Ber.*,32, 1921.
2. Van Damme, N., Zalisky, V., Lough, A. J., &Lemaire, M. T. (2015). Structure and magnetic properties of a cobalt (III) complex with redox-active 1-(2-pyridylazo)-2-phenanthrol (pap1). *Polyhedron*, *89*, 155-159.
3. Layek, M., Ghosh, M., Sain, S., Fleck, M., Muthiah, P. T., Jenniefer, S. J.,& Bandyopadhyay, D. (2013). Synthesis, crystal structure and magnetic properties of nickel (II) and cobalt (III) complexes of a pentadentate Schiff base. *Journal of Molecular Structure*, *1036*, 422-426.
4. Patange, V. N., & Arbad, B. R. (2011). Synthesis, spectral, thermal and biological studies of transition metal complexes of 4-hydroxy-3-[3-(4-hydroxyphenyl)-acryloyl]-6-methyl-2H-pyran-2-one. *J. Serb. Chem. Soc.*, *76(9)*, 1237-1246.
5. Shah, S.S., Goswami, K. (2014). Synthesis, characterization and biological activity of some novel chalcone compounds and their Cobalt and Nickel complexes having benzyloxy dibromo acetophenone moiety, *Der Pharmacia letter*,*6(3)*:304-312.
6. Kubaisi, A. A., & Ismail, K. Z. (1994). Nickel (II) and palladium (II) chelates of dehydroacetic acid Schiff bases derived from thiosemicarbazide and hydrazinecarbodithioate. *Canadian journal of chemistry*, *72(8)*, 1785-1788.
7. Deshmukh AJ, Patil RM, LokhandeRS, Ner DH, (2017)Synthesis, characterization and antimicrobial activity of copper (II) complexes of some 2-hydroxy-4, 5-dimethyl substituted chalcones, *International Journal of Advanced Research and Review*, *3(1)*, 27-31.
8. Shastri, R. A. (2015). Synthesis and Antimicrobial Activity of Some Novel Pyrazoline and Flavone Derivatives Derived From Furan Chalcones. *World Journal of Pharmaceutical Research*, *4*, 642-651.
9. Pournalimardan, O., Chamayou, A. C., Janiak, C., & Hosseini-Monfared, H. (2007). Hydrazone Schiff base-manganese (II) complexes: Synthesis, crystal structure, and catalytic reactivity. *Inorganica Chimica Acta*, *360(5)*, 1599-1608.
10. Chiara, Sulpizio., Simon, T.R., Muller, Zhang Qi., Brecker, Lothar., Rampal, Annte. (2016). Synthesis, Characterization and Antioxidant activity of Zn²⁺ and Cu²⁺ coordinated polyhydroxychalcone complexes, *Montash Chem.* *147*:1871-1881.
11. Ipper, S.N., Raut, N.K., Dixit, P.P., Kakade, G.K., (2018). Synthesis, spectral study and properties of (E)-3-(5-bromofuran-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one, *Journal of Pharma Research*, *7(10)*, 220-223.
12. Mane, P.S., Shirodkar, S.G., Chondhekar, T.K. (2002). *J. Indian Chem. Soc.*, *79(A)*, 154.
13. Habib, S. I., Shah, S., Aseer, N. N. M. A., & Kulkarni, P. A. (2011). Synthesis and characterization of cobalt (ii), nickel (ii), and copper (ii) complexes of some 2'-hydroxy chalcones. *J. Chem. Pharm. Res.*, *3*, 788-792.
14. Tabti, S., Djedouani, A., Aggoun, D., Warad, I., Rahmouni, S., Romdhane, S., & Fouzi, H. (2018). New Cu (II), Co (II) and Ni (II) complexes of chalcone derivatives: Synthesis,

X-ray crystal structure, electrochemical properties, and DFT computational studies.
Journal of Molecular Structure, *1155*, 11-20.

- 15.** Barry, A. L. (1991). Procedures and Theoretical Considerations for testing Antimicrobial Agents in agar media. *Antibiotics in laboratory medicine*.