

Synthesis and Characterization of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) Complexes of β -Diketone

NARENDRA A. BHISE, ASHWINI A. AGALE, SURESH T. GAIKWAD and ANJALI S. RAJBHOJ*

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431 004, India

*Corresponding author: Tel/Fax: +91 240 2403311; E-mail: anjali.rajbhoj@gmail.com

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It is well known that β -diketones are also formed through Baker-Venkatarman transformation. In the present case, 3-bromo-2-methylbenzoic acid reacts with *ortho*-hydroxyacetophenone at room temperature to yield ester. Ester on further Baker-Venkatarman transformation yields 1,3-diketone (L) *i.e.* 1-(3-bromo-2-methylphenyl)-3-hydroxy-3-(2-hydroxyphenyl)prop-2-en-1-one. Five complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with bidentate ligand (L), have been synthesized from reaction of the ligand (L) with respective metal nitrates. β -diketone exhibits keto-enol tautomerism, their keto-enol tautomerism was studied in solution by IR and NMR spectroscopy. Due to enolization β -diketone acts as ligand and hence used to synthesized Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes. The synthesized ligand has been characterized by elemental analysis, ^1H , ^{13}C NMR, LC-MS and FT-IR. The magnetic susceptibility and solution conductivity were also studied. The synthesized complexes were also studied antimicrobial screening.

Keywords: Baker-Venkatarman transformation, Metal complexes, Magnetic susceptibility, Solution conductivity, Antimicrobial activity.

INTRODUCTION

Coordination compounds are important in chemistry of transition elements; they play a vital role as they have electro-positive nature, which forms ions in which they are capable of binding donor atoms. There is a large amount of literature available, which specially deals with applications of these complexes as components of molecular devices or as precursors in the formation of various new materials. β -diketones and related ligands have been studied for more than a century and their ability to give rise to rich and interesting coordination chemistry is well documented [1-7]. β -Diketones and its metal complexes have played a vital role in coordination chemistry [8-10] and are being extensively studied in various aspects of industries such as organic electroluminescent technology, luminescent materials, biological processes and serve as suitable models for valuable information in the elucidation of enzymatic processes of biological relevance [11-16]. β -Diketones and their metal complexes also show antimicrobial, antimalarial, antitumor activities, antioxidant and insecticidal activity [17-20]. β -Diketones exist in the intramolecular hydrogen bonded keto-enol tautomers. Due to enolization β -diketones act as a ligand and form chelates with metals, hence used in the solvent extraction of metals [21]. Considering the above requirements, in this paper, we report the synthesis of five kinds of transition metal-diketone complexes with 1-(3-bromo-2-methylphenyl)-3-hydroxy-3-(2-hydroxyphenyl)prop-2-en-1-one as ligand (L).

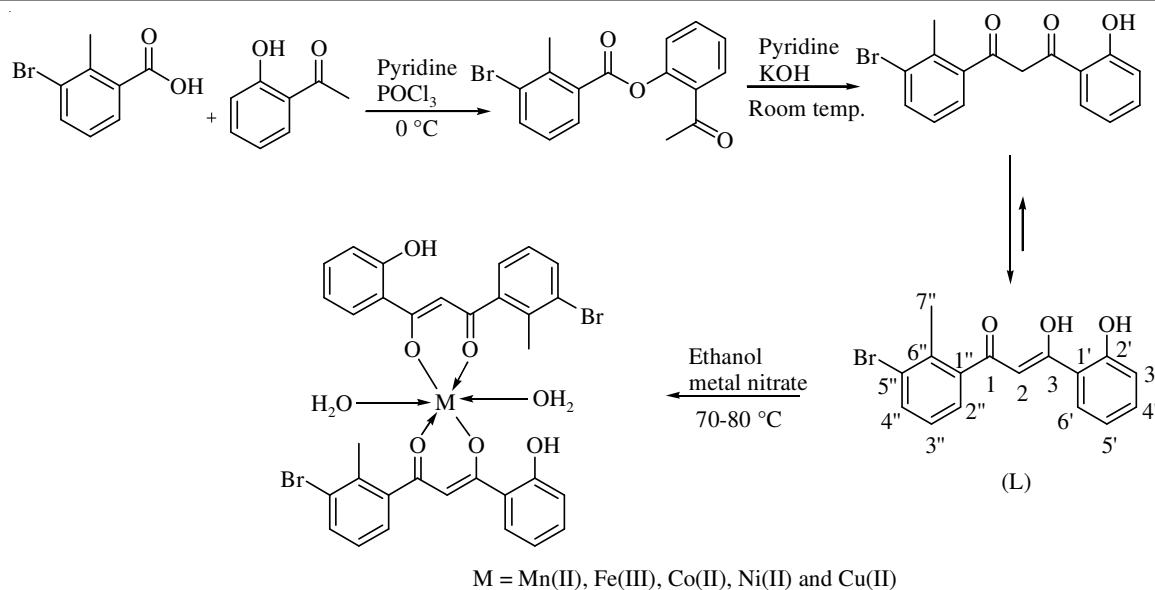
EXPERIMENTAL

Analytical grade chemicals were used for the synthetic work. Required chemicals were purchased from commercial sources and used without further purification. Distilled ethanol was used for recrystallization and complex preparation.

Synthesis of 2-acetylphenyl-3-bromo-2-methylbenzoate:

At room temperature, equimolar 3-bromo-2-methylbenzoic acid and *ortho*-hydroxyacetophenone was dissolved in pyridine and stirred for 15 min. To this reaction mixture POCl_3 were added drop wise at 0°C with constant stirring. The progress of reaction was monitored by TLC, after the completion of reaction, reaction mixture was poured on crushed ice and acidified with 1 M HCl. The obtained product was filtered on Buchner funnel and washed with water and recrystallized from ethanol to get chromatographically (TLC) pure compound. Yield: 80 % and m.p. 114°C .

Synthesis of 1,3-diketone (L): 2-Acetylphenyl-3-bromo-2-methylbenzoate was dissolved in 20 mL pyridine (5 g, 0.0141 mol) and to this solution pulverized KOH (3 g, 0.0424 mol) was added. The reaction mixture was stirred for 3 h and the progress of reaction was monitored by TLC during which time a copious precipitates of the yellow potassium salt of 1-(3-bromo-2-methylphenyl)-3-hydroxy-3-(2-hydroxyphenyl)prop-2-en-1-one formed (**Scheme-I**). After the completion of reaction, reaction mixture was poured on crushed ice and acidified with 1 M HCl. The obtained solid yellow product was filtered



Scheme-I: Synthesis of β -diketone (L) and its metal complexes

and recrystallized from ethanol to get chromatographically (TLC) pure product. Yield: 72 %, m.p. 119 °C.

Synthesis of metal complexes: All the complexes were synthesized by following the standard procedure. The complexes were prepared in 1:2 molar ratio *i.e.* metal to ligand. To a hot alcoholic solution of 1-(3-bromo-2-methylphenyl)-3-hydroxy-3-(2-hydroxyphenyl)prop-2-en-1-one, hot alcoholic metal nitrate solution were added. The resulting mixture was stirred and refluxed for 4 to 5 h whereupon the complex precipitation occurs after the addition of alcoholic ammonia. Solid mass was suction filtered, washed with ethanol and dried *in vacuo*.

Characterization: Melting points were determined in open glass capillaries and were uncorrected. Molar conductance of the complexes was measured in DMF (10^{-3} M) at room temperature by using Equiptronics Digital conductivity meter (EQ-660). The magnetic susceptibility of the complexes was measured at room temperature using a Guoybalance. The elemental analysis were carried out using EuroVector EA 3000 Elemental Analyzer, ^1H NMR and ^{13}C NMR were recorded on a Bruker's AVANCE-III 400 MHz FT-NMR spectrometers by using tetramethylsilane as an internal standard and CDCl_3 as solvent, FTIR were recorded using KBr disc on Shimadzu.

RESULTS AND DISCUSSION

All the synthesized transition metal complexes of ligand (L) were coloured, stable to air, insoluble in water but soluble

in polar solvent like DMF and DMSO. Magnetic moment and solution conductivity were measured at room temperature. Magnetic study reveals that the complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) were paramagnetic in nature, the molar conductance of complexes in 10^{-3} molar DMF solution are in the range $16\text{--}28 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating that, complexes are nonelectrolytic in nature [13]. The elemental data with their physical properties for the ligand and complexes were presented in Table-1. The analytical data of the complexes are in consistent with the molar ratio of 1:2 *i.e.* metal to ligand. The presence of two coordinated water molecules appears to be hexa-coordinated of metal atom and the probable geometry was octahedral.

^1H , ^{13}C NMR and Mass spectral data of ligand: The ^1H NMR and ^{13}C NMR spectra of the ligand was recorded in CDCl_3 are consistent with the proposed structure. ^1H NMR (CDCl_3) δ : 2.56 (s, 3H, $-\text{CH}_3$), 6.42 (s, 1H, $-\text{CH}=\text{C}$), 7.03–7.66 (m, 7H, Ar-H), 12.02 (s, 1H, Ar-OH), 15.21 (s, 1H, enolic-OH), ^{13}C NMR (400 MHz, CDCl_3) δ : 196.05 (s C-1, C=O), 97.36 (C-2, $-\text{CH}=\text{C}$), 180.11 (s, C-3), 118.66 (s, C-1'), 163.71 (s, C-2'), 118.89 (s, C-3'), 134.77 (s, C-4'), 119.21 (s, C-5'), 127.12 (s, C-6'), 136.34 (s, C-1''), 128.68 (s, C-2''), 127.66 (s, C-3''), 136.94 (s, C-4''), 126.88 (s, C-5''), 136.24 (s, C-6''), 20.73 (s, C-7'') LC-MS (ESI) at m/z 332.0.

FT-IR spectra: Fig. 1 shows the most important region of the infrared spectra and determines the ligand and metal mode of coordination. The IR spectra of free ligand and its metal complexes were measured and compared. The free ligand

TABLE-1
ANALYTICAL, PHYSICAL AND MOLAR CONDUCTANCE DATA OF THE COMPOUNDS

Ligand/Complex	f.w.	m.p. (°C)	Magnetic moment μ_{eff} (BM)	Molar conductance	Elemental analysis (%): Found (calcd.)			
					C	H	O	M
L	333.18	119	–	–	56.71 (57.68)	4.51 (3.93)	13.13 (14.41)	–
[Mn(L) ₂](H ₂ O) ₂	755.31	> 300	5.57	28.0	49.12 (50.33)	3.46 (3.74)	15.11 (16.50)	(7.27)
[Fe(L) ₂](H ₂ O) ₂	756.21	> 300	5.29	16.4	49.22 (50.82)	5.10 (3.73)	15.95 (16.93)	(7.38)
[Co(L) ₂](H ₂ O) ₂	759.3	> 300	3.12	18.11	50.05 (50.62)	4.70 (3.72)	14.12 (15.86)	(7.76)
[Ni(L) ₂](H ₂ O) ₂	759.06	> 300	2.15	23.58	51.90 (50.63)	4.13 (3.72)	14.53 (15.12)	(7.73)
[Cu(L) ₂](H ₂ O) ₂	763.91	> 300	0.82	25.23	52.59 (51.61)	3.38 (3.69)	15.75 (16.46)	(8.32)

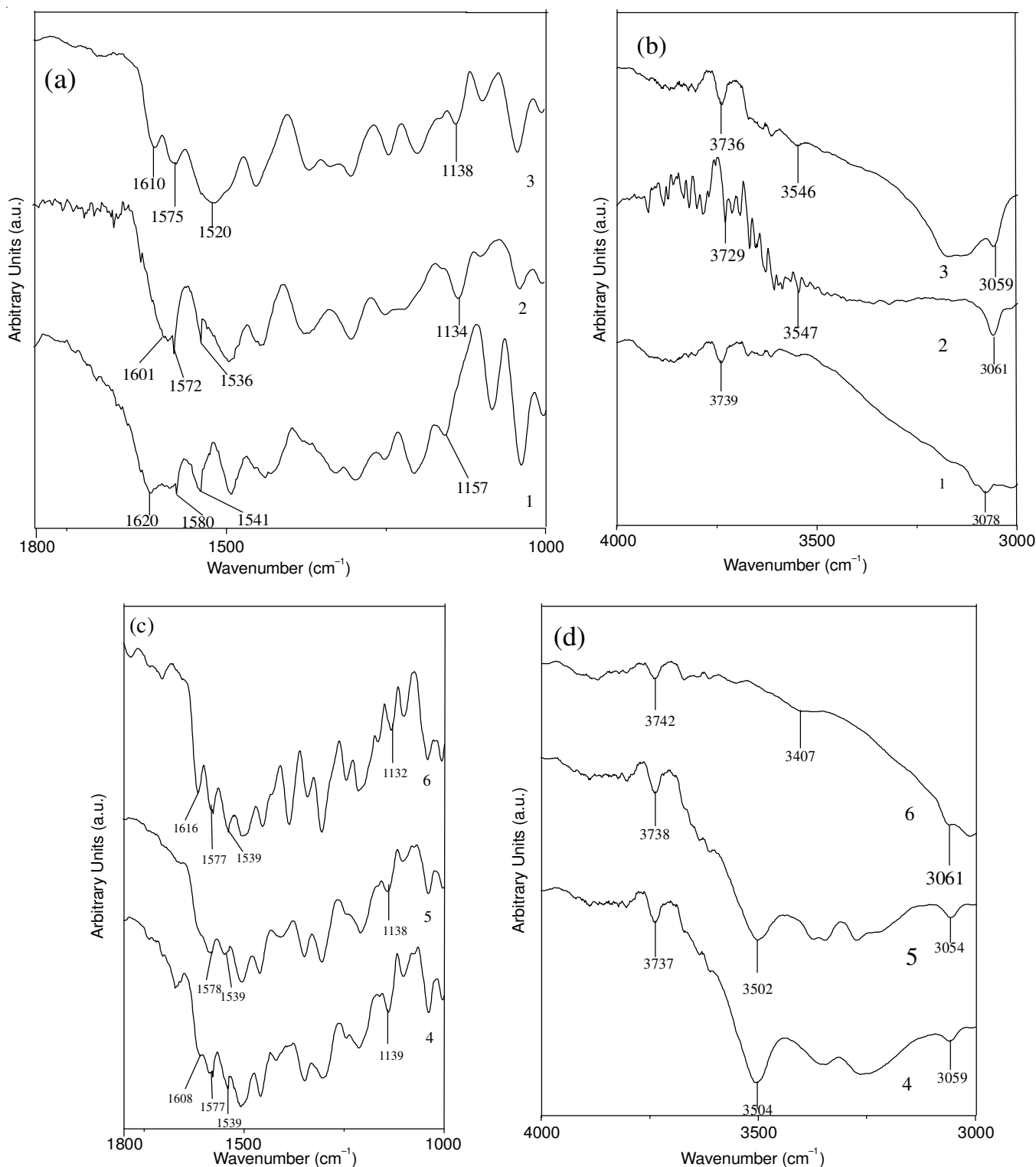


Fig. 1. FT-IR spectra of metal ligand and β -diketone complexes in solid: (a) & (c) 1000-1800 cm^{-1} ; (b) & (d) 3000-4000 cm^{-1} . 1 = ligand, 2 = $[\text{Mn}(\text{L})_2](\text{H}_2\text{O})_2$, 3 = $[\text{Fe}(\text{L})_2](\text{H}_2\text{O})_2$, 4 = $[\text{Co}(\text{L})_2](\text{H}_2\text{O})_2$, 5 = $[\text{Ni}(\text{L})_2](\text{H}_2\text{O})_2$ and 6 = $[\text{Cu}(\text{L})_2](\text{H}_2\text{O})_2$

β -ketone exhibits keto-enol tautomerism and shows a series of vibration bands at 1620, 1580, 1541, 1157 cm^{-1} which are attributed due to keto carbonyl $\nu(\text{C}=\text{O})$, enol carbonyl $\nu(\text{C}=\text{O})$, enol form $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{O})$ [22-24], respectively. It is noticeable that the peak appearing at 1620 due to $\nu(\text{C}=\text{O})$ vibration has been disappeared indicating that the β -diketone ligand act as an enol tautomer in the complex. In addition to this the characteristic band for free ligand shift to lower

frequency in metal complexes of β -diketone as shown in Fig. 2. This lower shifting is due to the loss of acidic proton from enolic hydroxyl moieties and bonding of both enol hydroxyl oxygen and enolic carbonyl oxygen to the metal ion in a chelate mode. So the enhanced conjugation from keto-enol tautomer to enolic form hexahydric chelate ring gives a natural interpretation of the lower frequency shifts seen experimentally in the complexes. In the IR spectra of (ii), there is a weak and broad

absorption at 3078 cm^{-1} in the free ligand which would be due to the unsaturated νCH stretching vibration of the aromatic ring, for metal β -diketone complexes, this band decreased in intensity and most likely originating from the metalation which increases the conjugation and delocalization of the aromatic ring with a neighboring enol form hexahydric ring. Moreover, in the spectrum of the complexes, a wide and strong band around $3547\text{--}3407\text{ cm}^{-1}$, which is not obviously seen with the free ligand. This appearance of absorption bands is assigned to $\nu(\text{OH})$ and $\rho_r(\text{OH})$ vibrations [25,26], showing that there are coordinated water molecules in the metal complexes. Therefore, the FT-IR spectra indicate that the metal complexes may prefer to form a hexa-coordinated form. These results agree well with that of elemental analytical data above Table-1 and TG analyses. The group of peaks centered at $3742\text{--}3729\text{ cm}^{-1}$ around in ligand and metal complexes due to atmospheric moisture (gaseous) molecules [27]. The IR spectra of the metal complexes of β -diketone are very similar, except some of the slight shift and intensity change of a vibration band caused by different metal ions.

X-ray diffraction studies: XRD patterns of Cu(II) and Ni(II) complexes of β -diketone shows well defined crystalline peaks (Fig. 2). The indexing and calculations of unit cell parameters were performed using powder-X software. Millere's indices and lattice constant were evaluated which corresponds to monoclinic system for the complexes. Table-2 deals with summary, refinement parameters and average crystallite size

for the above mentioned complexes was calculated using grain software.

Thermal properties of β -diketone metal complexes:

The simultaneous TG/DTA analysis of metal complexes was studied from ambient temperature to $1000\text{ }^\circ\text{C}$ in nitrogen atmosphere using $\alpha\text{-Al}_2\text{O}_3$ as reference (Fig. 3). Co(II) and Fe(III) complexes of ligand (L) were chosen for thermal study. The thermogram curve of Co(II) complex shows weight loss 4.65% (cal 4.74%) in the temperature range $65\text{--}190\text{ }^\circ\text{C}$ and sharp endotherm at $90\text{ }^\circ\text{C}$ which clearly indicate a removal of two coordinated water molecules. The anhydrous complexes first show slow decomposition from 200 to $475\text{ }^\circ\text{C}$, with 64.44% (cal 64.97%) mass loss, a broad exotherm with $435\text{ }^\circ\text{C}$ in the DTA may be attributed to the removal of non-coordinate part of ligand. The second step of the decomposition from 500 to $735\text{ }^\circ\text{C}$ with a mass loss of 21.36% (cal 21%) corresponds to the decomposition of the coordinated part of the ligand. A broad endothermic peak at $470\text{ }^\circ\text{C}$ in the DTA region was observed for this step. The mass of the final residue CoO , 7.549% (cal 8.865%) which is in agreement.

Thermogram of Fe(III) complex showed a mass loss 4.228% (cal 4.7646%) in the temperature range $35\text{--}250\text{ }^\circ\text{C}$ and sharp endotherm at $196\text{ }^\circ\text{C}$ which clearly indicate a removal of two coordinated water molecules. The anhydrous complex first show slow decomposition from 275 to $565\text{ }^\circ\text{C}$, with 53.81% (cal 54%) mass loss, a broad exotherm with $378\text{ }^\circ\text{C}$ in the DTA may be attributed to the removal of non-coordinate part

TABLE-2
SUMMARY OF XRD DATA AND REFINEMENT PARAMETERS OF COPPER AND NICKEL METAL COMPLEXES

Parameters		Cu(II) complex				Ni(II) complex					
Temperature		298				298					
Wavelength (\AA)		1.540598				1.540598					
Radiation		$\text{CuK}\alpha$				$\text{CuK}\alpha$					
Crystal system		Monoclinic				Monoclinic					
Unit cell dimension											
a (\AA)		12.307				12.6912					
b (\AA)		13.5489				15.5434					
c (\AA)		8.7457				10.7214					
α ($^\circ$)		90				90					
β ($^\circ$)		96				94					
γ ($^\circ$)		90				90					
Average particle size (nm)		8.9546300				21.62117233					
Cu(II) complex						Ni(II) complex					
h k l	2θ (exp)	2θ (cal)	d spacing (exp)	d spacing (cal)	Intensity (exp)	h k l	2θ (exp)	2θ (cal)	d spacing (exp)	d spacing (cal)	Intensity (exp)
-1 0 0	7.367	7.217	11.99029	12.23958	1987.97	0 2 0	11.399	11.377	7.75668	7.77170	2580.21
0 2 0	12.905	13.058	6.85455	6.77445	997.47	1 1 1	12.331	12.555	7.17197	7.04461	2502.19
-2 0 0	14.452	14.462	6.12417	6.11979	2011.00	0 2 1	14.460	14.075	6.12083	6.28712	3166.10
0 2 1	16.593	16.573	5.33839	5.34459	1254.50	-1 2 1	15.536	15.464	5.69916	5.72530	2880.57
-2 1 1	17.954	18.043	4.93651	4.91240	1485.65	-2 0 1	15.819	15.750	5.59769	5.62212	2565.40
-2 2 0	19.420	19.532	4.56716	4.54120	1859.09	-2 1 1	16.833	16.756	5.26286	5.28690	1907.01
0 0 2	20.329	20.405	4.36502	4.34889	1578.57	0 3 1	18.815	19.018	4.71271	4.66282	1850.11
-1 1 2	21.981	21.497	4.04052	4.04659	1459.32	2 2 1	20.348	20.295	4.36080	4.37206	1545.38
1 3 1	23.639	23.669	3.76076	3.75599	1196.67	3 0 1	23.107	23.173	3.84608	3.83528	4223.70
-1 2 2	24.884	24.751	3.57528	3.59416	1085.07	1 4 0	23.940	23.935	3.71404	3.71480	1521.05
1 2 2	26.140	25.998	3.40633	3.42461	1274.24	-3 2 1	24.887	24.905	3.57483	3.57238	6651.80
1 4 0	27.362	27.297	3.25685	3.26452	1511.61	3 2 1	25.911	25.885	3.43590	3.43928	8832.88
0 4 1	28.085	28.251	3.17464	3.15633	1046.83	1 0 3	26.500	26.420	3.36076	3.37083	1795.19
2 2 2	29.499	29.496	3.02565	3.02586	1043.50	-2 3 2	27.148	27.181	3.28201	3.27816	3310.90
-	-	-	-	-	-	3 0 2	27.750	27.806	3.21224	3.20583	2583.10

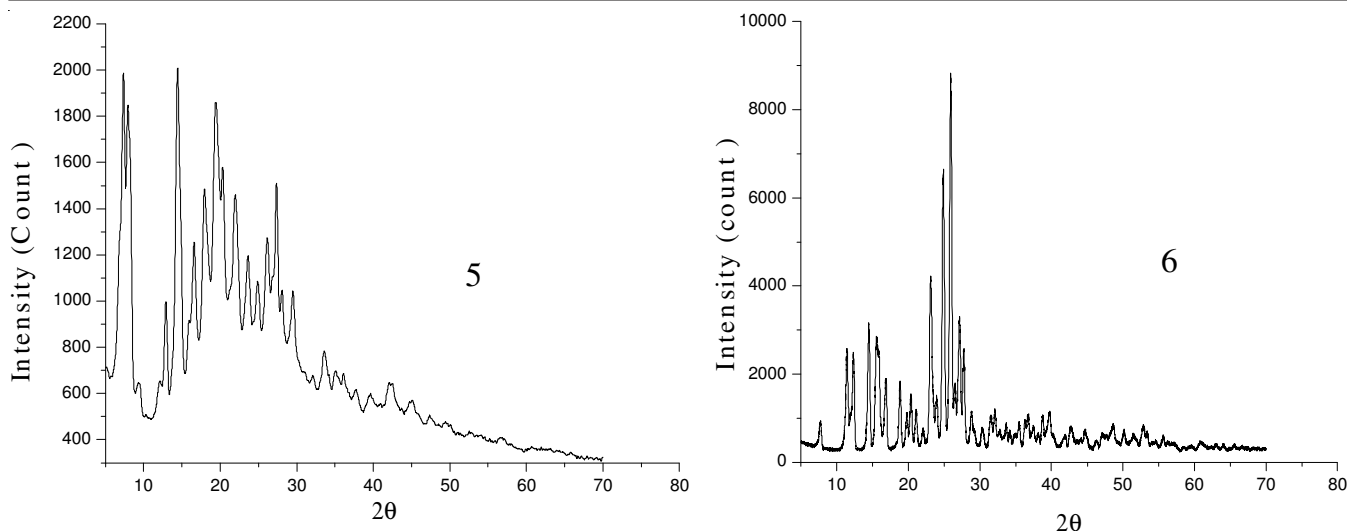


Fig. 2. XRD Patterns: compound **5** = $[\text{Ni}(\text{L})_2](\text{H}_2\text{O})_2$ and compound **6** = $[\text{Cu}(\text{L})_2](\text{H}_2\text{O})_2$

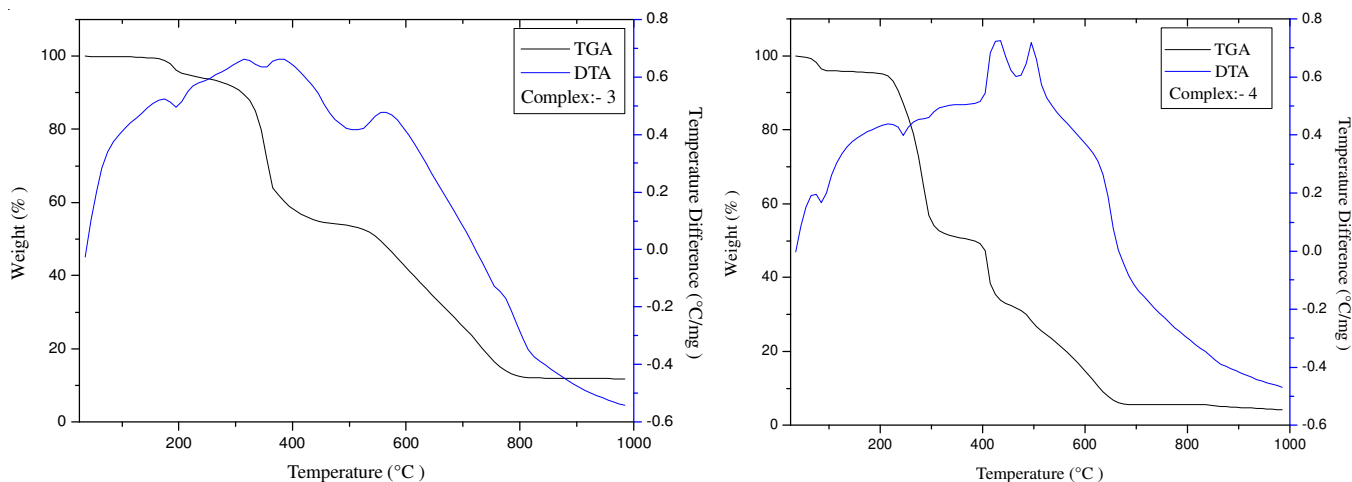


Fig. 3. TGA-DTA curves of compound **3** = $[\text{Fe}(\text{L})_2](\text{H}_2\text{O})_2$ and compound **4** = $[\text{Co}(\text{L})_2](\text{H}_2\text{O})_2$

of ligand. The second step of the decomposition from 575 to 835 °C with a mass loss of 21.36 % (cal 20 %) corresponds to the decomposition of the coordinated part of the ligand. A broad endothermic peak at 470 °C in the DTA region was observed for this step. The mass of final residue of Fe_2O_3 , 20.86 % (theoret. 1 21.114) was in good agreement.

Antimicrobial screening: In this work Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) metal complexes of ligand (L) have been explored for their antibacterial and antifungal properties. The antimicrobial analysis was done on petri-plates containing solidified 20 mL Muller Hinton agar medium. These plates were inoculated with 20-24 h culture of bacterial and fungal strains. The antimicrobial activity was assayed by measuring the diameter of the inhibition zone formed in terms of mm.

The study of antibacterial and antifungal activities of β -diketone ligand and its metal complexes have been carried out on three bacteria *Salmonella typhimurium*, *Pseudomonas aeruginosa* and *Klebsiella Pneumoniae* at 250 and 500 ppm and two fungi *Saccharomyces cerevisiae* and *Candida albicans* at 10 ppm and using gentamycin and amphotericin B as positive control reference drugs in antibacterial and antifungal activity assay, respectively.

in vitro Antibacterial evaluation: In case of *K. pneumoniae* only cobalt complex was found to be moderately active compared to positive control (gentamycin), while rest of the compounds did not show activity for it. The antibacterial activity of Ni complex was found to be better than rest of the compounds against *S. typhi* and *P. aeruginosa*, while Fe(III) complex does not show activity for it.

in vitro Antifungal evaluation: *in vitro* Antifungal screening data suggested that among the tested compounds iron, cobalt and copper complexes against *Saccharomyces cerevisiae* and ligand and nickel complexes against *Candida albicans* did not show activity while rest of the compounds shown sound bacterial activity than positive control (amphotericin B). Nickel complex showed the highest activity against *Saccharomyces cerevisiae* and manganese showed the highest activity against *Candida albicans*.

A comparative study of the synthesized metal complexes exhibited promising antimicrobial activity as compared to free ligand (L) as reported earlier [28]. The enhanced activity of the complexes can be explained on the basis of Tweedy's chelation theory [29]. The polarity of metal ion reduced considerably on chelation because of the partial sharing of its

TABLE-3
MICROBIAL SCREENING OF LIGAND AND ITS METAL COMPLEXES

Compound	Mean zone of inhibition diameter \pm SD (mm)							
	Antibacterial screening						Antifungal screening	
	<i>S. typhi</i>		<i>P. aeruginosa</i>		<i>K. pneumonia</i>		<i>S. cerevisiae</i>	<i>C. albicans</i>
	250 ppm	500 ppm	250 ppm	500 ppm	250 ppm	500 ppm	10 ppm	10 ppm
L	11.00 \pm 2.00	13.00 \pm 2.00	10.00 \pm 2.00	12.33 \pm 2.51	0.00 \pm 0.00	0.00 \pm 0.00	10.00 \pm 1.00	0.00 \pm 0.00
[Mn(L) ₂](H ₂ O) ₂	14.66 \pm 0.57	16.00 \pm 1.00	13.33 \pm 1.52	15.33 \pm 1.52	0.00 \pm 0.00	0.00 \pm 0.00	11.00 \pm 1.00	15.20 \pm 1.30
[Fe(L) ₂](H ₂ O) ₂	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	14.03 \pm 1.94
[Co(L) ₂](H ₂ O) ₂	13.00 \pm 1.00	16.33 \pm 1.52	11.66 \pm 1.15	14.00 \pm 1.00	13.00 \pm 1.73	14.33 \pm 2.51	0.00 \pm 0.00	12.32 \pm 2.50
[Ni(L) ₂](H ₂ O) ₂	22.44 \pm 0.51	25.55 \pm 1.26	15.78 \pm 2.28	17.66 \pm 0.57	0.00 \pm 0.00	0.00 \pm 0.00	12.29 \pm 0.60	0.00 \pm 0.00
[Cu(L) ₂](H ₂ O) ₂	16.18 \pm 0.74	19.00 \pm 2.00	11.00 \pm 2.00	13.08 \pm 2.12	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	7.00 \pm 1.00
Gentamycin	26.37 \pm 0.54	27.44 \pm 0.76	26.37 \pm 1.18	29.54 \pm 1.50	28.51 \pm 1.50	29.42 \pm 1.41	–	–
Amphotericin B	–	–	–	–	–	–	4.66 \pm 0.577	2.33 \pm 0.57

SD = Standard deviation; Test applied- One way ANOVA with post hoc Tukey HSD test

positive charge with the donor atoms of the ligand and also due to π -electron delocalization over the whole chelate ring system. The polysaccharides and lipids are the important constituents of the cell wall and membranes, which are favourable for metal ion interaction. Besides this, cell walls also constitute carbonyl, phosphate and cystenyl ligands, which help in maintaining the integrity of the membrane by performing as a diffusion barrier and also provide suitable sites for binding [30]. Moreover, the reduction in polarity enhances the lipophilic character of the chelates and an interaction between the lipid and metal ion is favoured. This may lead to the breakdown of the permeability barrier of the cell resulting in intervention with the normal cell processes and blocking of the metal binding sites in the enzymes of the microorganisms. These complexes may also disturb the respiration process of the cell and therefore block the protein synthesis, which confines further growth of the organism [31].

The antimicrobial data have been analyzed by data analysis tool [32]. One way ANOVA followed by the Tukey' HSD test. The obtained statistical results of biological studies of β -diketone and its metal complexes against bacteria and fungi were tabulated in Table-3. The results obtained from Tukey' HSD test strongly suggest that statistically significant different occur in antimicrobial screening.

Conclusion

β -Diketones 1-(3-bromo-2-methylphenyl)-3-hydroxy-3-(2-hydroxyphenyl)prop-2-en-1-one have been synthesized from Baker-Venkataraman transformation of 2-acetylphenyl-3-bromo-2-methylbenzoate. Their transition metal complexes have been prepared and characterized by physical, spectral and analytical data. The functionalized β -diketone potentially acts as bidentate ligand and coordinate with the transition metal atom through β -diketo system. The complexes have general formula $[M(L)_2](H_2O)_2$ where M = Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and L = ligand. Ligand L and their transition metal complexes have been screened for *in vitro* antibacterial and antifungal. The biological activity data show that the transition metal complexes are more potent antibacterial and antifungal agents than the parent β -diketone against different bacterial and fungal species. This constitutes a new group of compounds that can be used as potential metal derived drugs. The metal complexes were also studied for their thermogravimetric analyses.

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