Ultrasound Synthesis, Characterization and Thermal Study of Some Transition Metal Complexes of B – Diketone Ligand

Nanda S. Korde, Suresh T. Gaikwad, Seema S. Korde, Anjali S. Rajbhoj

Abstract: Complexes of Fe(III), Co(II), Ni(III), Cu(II) and Cr(III) with cyclic β-diketone ligand were synthesized by ultrasound irradiation and characterized by elemental analysis, conductometry, magnetic susceptibility, UV-Vis, IR, 1H-NMR, 13C-NMR, X-ray diffraction analysis of powdered samples thermal analysis, and screened for antimicrobial activity. The IR spectral data suggested that the ligand behaves as a bidentate ligand towards the central metal ion with an O-O,O-O donor atoms sequence. From the microanalytical data, the stoichiometry of the complexes 1:2 (metal : ligand) was found. The physico-chemical data suggested octahedral geometry for all these complexes. The thermal behavior (TGA/DTA) of the complexes were studied and kinetic parameters were determined by Horowitz- Metzer method. The powder X-ray diffraction data suggested a monoclinic crystal system for the Fe(III) and Co(II) complexes. The ligand and their metal complexes were screened for antibacterial activity against Staphylococcus aureus, B. subtilis and E. coli and fungicidal activity against A. niger and F. oxysporum.

Keywords: Cyclic β-diketone; Baker-Venkatraman transformation; transition metal complexes; ultrasoun irradiation; XRD; Thermal analysis; antimicrobial activity

I.INTRODUCTION

β-diketone and its metal complexes have been widely used in diverse areas because of their unique structural features, chemical functionalities, and toughness for light and heat as electroluminescence materials.[1] Cyclic β-diketones have gained a lot of interest due to their importance as good ligands[2] for the chelation with metals, as intermediate in the synthesis of core heterocycles such as flavones,[3] benzodiazepine,[4] pyrazole,[5] isoxazole[6] and pyrimidine[7] and triazole.[8] β-diketones are well known to have keto-enol tautomerism[9] and recently it is reported that they have the important pharmacophores for the HIV-integrase(1N) inhibitors.[10] Further, it has been reported recently that a number of β-diketones has warrant examination as breast cancer chemopreventative blocking agent,[11] anticarcinogenic agent[12] and antiestrogenic agent.[13] In this paper, we report a new route for the synthesis of iron complexes of cyclic β-diketones.

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A search of the literature revealed that no work has been done on transition metal complexes of the 1-(2-hydroxyphenyl)-3-(4-bromoyphenyl)propane-1,3-dione. The synthesis of 1-(2-hydroxyphenyl)-3-(4-bromophenyl) propane-1,3-dione formed by rearrangement of 2-acetylphenyl benzoate employing Baker-Venkatraman transformation by ultrasound irradiation. The complexes of Fe(III), Co(II), Ni(II), Cu(II) and Cr(III) with this ligand were also prepared in the solid state by ultrasound irradiation and characterized by different physico-chemical methods.

II.EXPERIMENTAL

All ^{1}H-NMR and ^{13}C-NMR spectras were recorded in $CDCl_3$ using TMS as the internal standard. FT-IR spectra were recorded using(KBr) disc on Bruker spectro-photometer. Mass spectra were taken on a Macro mass spectrometer. The TG/DT curves and XRD patterns were recorded on a Perkin Elmer TA/SDT-2960 and a Philips 3701, respectively. The UV-Vis spectra of the ligand and complexes were recordrd on a Shimadzu UV-1601 spectrometer. The magnetic susceptibility measurements of the metal chelates were determined on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as the calibrant. The molar conductance of the complexes were measured on an Elico CM 180 conductivity meter using 10^{-3}M solutions in DMF. The antimicrobial activity were carried from the Microbiology Department, Dayanand Science College, Latur. All chemicals used were of AR grade. Melting points were determined in open glass capillaries and were uncorrected. Purity of the products were checked by TLC.

Synthesis

The β-diketone ligand was synthesized via a stepwise approach. In the first step, 2-acetylphenyl benzoate was prepared by stirring mixture of o-hydroxyacetophenone (1.36g, 0.01mol), 4-bromo benzoic acid (2.01g, 0.01mol), a dry pyridine (5ml) and $POCl_3$ (1 ml) at 0ºC. The reaction mixture was stirred for about 8-9 hr.at room temperature. After completion of the reaction (monitored by TLC) , the reaction mixture was poured into 100ml HCl (1M) containing 50g of crushed ice and solid obtained was recrystallized from ethanol, filtered and dried. Yield: 72% , m.p. 108°C.Thus formed 2-acetylphenyl benzoate was dissolved in dry pyridine (10 mL). To this powdered KOH (1.12g, 0.02mol) was added and the reaction mixture was irradiated for about 2-3 hr. under ultrasound.

After completion of reaction (monitored by TLC), the reaction mixture was poured on ice cold water and acidified with conc.HCl. The yellow solid of the 1-(2-hydroxyphenyl)-3-(4-bromoyphenyl)propane-1,3-dione obtained was filtered off and crystallized from absolute ethanol.Yield: 87%, m.p.130°C.

Compound	F.W.	M. P. °C	Colour	Λ S cm^2 mol^{-1}	Found (Calcd.)%			
					C	H	O	M
$C_{15}H_{11}O_3Br$	319	130	Yellow		56.45 (56.09)	3.47 (3.20)	15.04 (14.86)	-------
$C_{32}H_{32}FeBrO_{10}$	727	330	Brown	67.2	49.48 (49.41)	3.32 (3.15)	17.58 (17.04)	7.67 (7.01)
$C_{32}H_{32}CoBrO_{10}$	733	258	Reddish brown	30.6	49.27 (49.11)	3.31 (3.22)	17.50 (17.35)	8.06 (7.35)
$C_{32}H_{32}NiBrO_{10}$	733	215	Light green	38.8	49.29 (49.13)	3.31 (3.12)	17.15 (17.18)	8.03 (7.85)
$C_{32}H_{32}CuBrO_{10}$	738	232	Green	31.9	48.97 (47.89)	3.29 (3.11)	17.39 (17.01)	8.64 (8.44)
$C_{32}H_{32}CrBrO_{10}$	726	295	Dark brown	31.7	49.75 (48.81)	3.34 (3.03)	17.67 (17.02)	7.18 (6.73)

To a hot methanolic solution (15ml) containing 2.0 mmol (0.63g) of the ligand, a methanolic solution (15ml) of a metal nitrate (hydrate) (1.0 mmol) was added under constant stirring. The pH of the reaction mixture was adjusted to 7.5-8.5 by adding 10% alcoholic ammonia solution and irradiated about 1-2hrs under ultrasound. The precipitated solid metal complex was filtered off under hot conditions and washed with hot methanol, petroleum ether (40-60°C) and dried over anhydrous CaCl$_2$ in a vacuum desiccators (yield: 81-88%).

Antimicrobial activity

The antibacterial screening of synthesized compounds was carried out by paper disc diffusion[14] method at 100ppm against Gram +ve bacteria B. subtilis, S. aureus and Gram –ve bacteria E. coli. The compounds were tested at the concentration 100ppm in DMSO and compared with known antibiotics viz streptomycin. The antifungal activity of the compounds were assayed using fungal species Aspergillus niger and F. Oxysporum. Standard antibacterial streptomycin also screened under similar condition for comparison.

III. RESULTS AND DISCUSSION

The physical characteristics, microanalytical, and molar conductance data of the ligand and its metal complexes are given in Table I. The analytical data of the complexes revealed 1:2 mole ratio (metal:ligand) and corresponds well with the general formula [ML$_2$(H$_2$O)$_2$] (M = Fe(III), Co(II), Ni(II), Cu(II) and Cr(III)). The magnetic susceptibilities of all complexes at room temperature were found to be consistent with octahedral geometry having two water molecules coordinated to the metal ion. The presence of two coordinated water molecules was confirmed by TG/DT

analysis. The metal chelate solutions in DMF showed low conductance, supporting the non-electrolyte nature of the complexes.

TABLE I. Physical characterization and analytical and molar conductance data of the prepared compounds

Compound	F.W.	M. P. °C	Colour	Λ S cm^2 mol^{-1}	Found (Calcd.)%			
					C	H	O	M
$C_{15}H_{11}O_3Br$	319	130	Yellow		56.45 (56.09)	3.47 (3.20)	15.04 (14.86)	-------
$C_{32}H_{32}FeBrO_{10}$	727	330	Brown	67.2	49.48 (49.41)	3.32 (3.15)	17.58 (17.04)	7.67 (7.01)
$C_{32}H_{32}CoBrO_{10}$	733	258	Reddish brown	30.6	49.27 (49.11)	3.31 (3.22)	17.50 (17.35)	8.06 (7.35)
$C_{32}H_{32}NiBrO_{10}$	733	215	Light green	38.8	49.29 (49.13)	3.31 (3.12)	17.15 (17.18)	8.03 (7.85)
$C_{32}H_{32}CuBrO_{10}$	738	232	Green	31.9	48.97 (47.89)	3.29 (3.11)	17.39 (17.01)	8.64 (8.44)
$C_{32}H_{32}CrBrO_{10}$	726	295	Dark brown	31.7	49.75 (48.81)	3.34 (3.03)	17.67 (17.02)	7.18 (6.73)

1H-NMR spectrum of the ligand

The ^{1}H-NMR spectra of the free ligand in the CDCl$_3$ at room temperature showed the following signals at δ (ppm): 6.8 (d,3H,Ar-H), 7.7 (m, Ar-H), 7.39 (s,1H, =CH-) , 12.1 (s,1H, phenolic OH), 15.5 (s, 1H, Enolic-OH).

13C-NMR spectrum of the ligand

The ^{13}C-NMR spectra of the free ligand in the CDCl$_3$ at room temperature showed the following signals at δ 190.0(s,C-1,C=O), 93.0(s,C-2,-CH=), 184.2(s,C-3), 126.5(s, C-1'), 162.0(s,C-2'), 119.0(s,C-3'), 136(s,C-4'), 119.5(s,C-5'), 131.3(s,C-6'), 129.4(s,C-1''), 128.6(d,C-2'',C-6''), 131.6(d,C-3'',C5''), 122.3(s,C-4'').

The ^{1}H-NMR spectrum of ligand exhibited a singlet at δ15.5 ppm due to enolic proton (since enol form in β-diketone is more stable) , a singlet at δ12.1 ppm due to phenolic proton adjacent to the carbonyl group whereas ^{13}C-NMR spectra gives singlet at δ190.0 ppm due to ketonic carbon C-1 and δ184.2 ppm due to enolic carbon C-3 confirming the formation of β-diketone and the keto-enol tautomerism.

IR spectra

The IR spectrum of free ligand showed characteristic bands at 3069.78 (-OH), 1702.02 (C=O), 1486.96 (Ar C=C). The IR spectra of the metal chelates showed new bands in the 561.69-657.62 cm-1 regions, which can be assigned to ν(M-O)15 vibrations. The C=O bond in complex shifted to lower frequency as compared to that of free ligand which indicates the coordination of metal atom with the carbonyl group of diketone. The IR spectra of all complexes show a strong band in the 3180-3578 cm-1 region, indicating the presence of coordinated water in these complexes.

The presence of coordinated water was further confirmed by the appearance of a non-ligand band in the 825-850 cm-1 region, assignable to the rocking mode of water.[16] The presence of coordinated water was also established and supported by TG/DT analysis of these complexes.

Magnetic measurements and electronic absorption spectra

The magnetic and electronic spectral data are given in Table II. The electronic absorption spectrum of the Fe(III) complex in DMSO solution showed three bands at 18426, 22195 and 26292 cm^{-1}, assignable to the transitions $^6A_{19} \rightarrow T_1(D)$, $^6A_{19} \rightarrow {}^4T_1$ and $^6A_{19} \rightarrow {}^4T_{29}$ respectively. These data and the magnetic moment value of 5.52 (B.M.) suggest high-spin octahedral geometry.[17] The electronic absorption spectrum of the Co(II) complex in DMSO solution consisted of three bands at about 10820, 18001 and 20132 cm^{-1}, assigned to $^4T_{1g} \rightarrow {}^4T_{2g}(F)$, $^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions respectively. These data and magnetic moment value of 4.06 (B.M.) indicates the presence of Co(II) complexes in octahedral geometry.[18] The electronic absorption spectrum of the Ni(II) complex showed three bands at 13120, 16615 and 24920 cm^{-1} assigned to the spin-allowed transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, respectively. These data and magnetic moment value of 3.08 (B.M.) consistent with their well-defined octahedral configuration.[19] The electronic absorption spectrum of the Cu(II) complex showed three bands at 10559, 16528 and 24449 cm^{-1} which are assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2E_g$ transitions. These data and magnetic moment value of 1.88 (B.M.) suggest distorted octahedral geometry.[20-21] The electronic absorption spectrum of the Cr(III) complex in DMSO solution consisted of three bands at about 16780, 23902 and 35030 cm^{-1} which are assigned to $^4A_{2g} \rightarrow {}^4T_{2g}(F)$, $^4A_{2g} \rightarrow {}^4T_1(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transitions respectively. These data and magnetic moment value of 3.68 (B.M.) suggest octahedral geometry.[22]

TABLE II. Magnetic and electronic absorption spectral data (in DMSO) of the compounds

Compound	μ_{eff} (B.M.)	ν/ cm^{-1}	Band assignment	Geometry
C$_{32}$H$_{32}$FeBrO$_{10}$	5.52	18426 22195 26292	$^6A_{19} \rightarrow T_1(D)$ $^6A_{19} \rightarrow {}^4T_1$ $^6A_{19} \rightarrow {}^4T_{29}$	Octahedral
C$_{32}$H$_{32}$CoBrO$_{10}$	4.06	10820 18001 20132	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$ $^4T_{1g} \rightarrow {}^4A_{2g}(F)$ $^4T_{1g} \rightarrow {}^4T_{1g}(P)$	Octahedral
C$_{32}$H$_{32}$NiBrO$_{10}$	3.08	13120 16615 24920	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
C$_{32}$H$_{32}$CuBrO$_{10}$	1.88	10559 16528 24449	$^2B_{1g} \rightarrow {}^2A_{1g}$ $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2E_g$	Octahedral
C$_{32}$H$_{32}$CrBrO$_{10}$	3.68	16780 23902 35030	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$ $^4A_{2g} \rightarrow {}^4T_1(F)$ $^4A_{2g} \rightarrow {}^4T_{1g}(P)$	Octahedral

Thermal analysis

The simultaneous TG/DT analysis of the Fe(III), Co(II), Ni(II) and Cu(II) metal complexes were studied from ambient temperature to 1000°C under nitrogen atmosphere using α-Al2O3 as the reference. The thermogram curve of Fe(III) complex shows weight loss 7.40% (calcd. 7.78%) in the temperature range 185-200°C and sharp endotherm at 190°C clearly indicate removal of two coordinated water molecules. The anhydrous complex exhibited a single step decomposition from 210°C to 820°C with 70% mass loss and a broad endothermic peak in the DTA. The Fe2O3 is obtained as the end product.[23]

The TG curve of Co(II) complex shows a mass loss of 8.65% (calcd. 8.28%) in the temperature range 190-220°C and endothermic DTA peak in the region 200°C, indicates the loss of two coordinated water molecules.[24] The anhydrous complex first showed decomposition from 235-545°C, with a 21.10% (calcd. 21.70%) mass loss and a broad exothermic peak with 250°C in the DTA, which may be attributed to the removal of the non-coordinated part of the ligand. The second step of the decomposition from 560-850°C, with a mass loss of 55.00% (55.65%) correspond to the decomposition of the coordinated part of the ligand. A broad endothermic peak in the DTA was observed for this step. The mass of the final residue CoO, 13.55% (calcd. 14.80%). The TG curve of Ni(II) complex shows a mass loss of 6.88% (calcd. 6.42%) in the temperature range 155-190°C and endothermic DTA peak in the region 170°C, indicates the loss of two coordinated water molecule. The anhydrous complex first showed decomposition from 360°C to 410°C, with a 24.50% (calcd. 22.70%) mass loss and a broad exothermic peak with 350°C in the DTA, which may be attributed to the removal of the non-coordinated part of the ligand. The second step of the decomposition from 460-890°C, with a mass loss of 56.30% (calcd.55.65%) corresponds to the decomposition of the coordinated part of the ligand.[25] A broad endothermic peak in the DTA was observed for this step. The mass of the final residue NiO, 18.02% (calcd.17.80%).

The TG curve of Cu(II) complex shows weight loss 7.40% (calcd. 7.18%) in the temperature range 185-200°C and sharp endotherm at 190°C clearly indicate removal of two coordinated water molecules. [26] The anhydrous complex first showed decomposition from 250-550°C, with a 23.10% (calcd. 22.70%) mass loss and a broad exothermic peak with 380°C in the DTA, which may be attributed to the removal of the non-coordinated part of the ligand. The second step of the decomposition from 600-850°C, with a mass loss of 55.95 % (55.65%) correspond to the decomposition of the coordinated part of the ligand. A broad endotherm in DTA was observed for this. The mass of final residue corresponds to stable CuO, 17.85% (calcd.16.05%).

Kinetic calculation

The kinetic and thermodynamic parameters viz. the order of reaction (n), the energy of activation (Ea), the pre-exponential factor (Z), the entropy of activation (ΔS#) and the Gibbs energy change (ΔG#), together with the correlation coefficient (r) for the non-isothermal decomposition of the metal complexes, were determined by the Horowitz-Metzer (HM) approximation method.[27] The obtained data are given in Table III.

The calculated values of the activation energy of the complexes are relatively low, indicating the autocatalytic effect of the metal ion on the thermal decomposition of the complex.28 The negative activation entropy value indicates that the activated complexes were more ordered than the reactant and that the reactions were slow. The more ordered nature may be due to the polarization of bonds in the activated state, which might occur through charge transfer electronic transitions.

TABLE III. The kinetic parameter of degradation of the metal complexes calculated by the Horowitz-Metzer (HM) method

Complex	Step	n	$Ea\ KJmol^{-1}$	$Z\ s^{-1}$	$\Delta S^{\#}\ JK^{-1}\ mol^{-1}$	$\Delta G^{\#}\ KJmol^{-1}$	Corelation coefficient(r)
$C_{32}H_{32}FeBrO_{10}$	I	1.5	39.40	5.1×10^{4}	-138.8	46.46	0.9948
	II	1.3	37.52	3.2×10^{7}	-198.6	52.04	0.9982
	III	0.99	32.62	6.7×10^{9}	-238.5	59.11	0.9951
$C_{32}H_{32}CoBrO_{10}$	I	1.1	37.16	0.7368	-253.3	30.77	0.9855
	II	0.95	12.53	4.290	-242.7	62.93	0.9995
$C_{32}H_{32}NiBrO_{10}$	I	0.85	136.36	8.7×10^{11}	-22.99	138.1	0.9909
	II	1.05	47.17	68.1×10^{12}	-219.3	71.92	0.9977
$C_{32}H_{32}CuBrO_{10}$	I	1.4	46.80	2.6×10^{4}	-179.0	57.12	0.9878
	II	1.2	40.76	4.8×10^{4}	-247.0	62.69	0.9922

Powder X-ray diffraction analysis

The X-ray diffractograms of the Fe(III), Co(II) and Cu(II) complexes were scanned in the range 10-90° at wavelength of 1.54Å. The diffractograms and associated data depict the 2Ө value of each peak, the relative intensity and interplanar spacing (d-values). The X-ray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10% were indexed using a computer programme.29 This indexing method also yields the Miller indices (hkl), the unit cell parameters and the unit cell volume. The unit cell of Fe(III) complex yielded values of lattice constants: a = 4.12Å, b = 8.55Å and c = 8.90Å, and a unit cell volume V = 313.51Å3. The unit cell of Co(II) complex yielded values of lattice constants: a = 8.134, b = 3.16Å and c = 6.75Å, and a unit cell volume V = 177.89Å3. The unit cell of Cu(II) complex yielded values of lattice constants: a = 10.10, b = 3.12Å and c = 6.20Å, and a unit cell volume V = 195.37Å3. In concurrence with these cell parameters, conditions such as a ≠ b ≠ c and α = γ = 90° ≠ β required for a monoclinic samples were tested and found to be satisfactory. Hence it can be concluded that the Fe(III), Co(II) and Cu(II) complexes were monoclinic crystal systems. The experimental density values of the complexes were determined using the specific gravity method30 and found to be 4.0921, 4.1303 and 3.2979 g cm-3 for the Fe(III), Co(II) and Cu(II) complexes respectively. Using the experimental density values, ρ, the molecular weight of the complexes, M, Avogadro's number, N, and the volume of unit cell, V, the number of molecules per unit cell were calculated using the equation $\rho = nM/NV$ and they were found to be two for Fe(III), one for Co(II) and four for Cu(II) complexes. With these values, the theoretical densities were computed and found to be 4.0443, 4.1700 and 3.3155 g cm-3 for the respective complexes. Comparison of experimental and theoretical density value shows good agreement within the limits of experimental error.31

Antimicrobial activity

The results of the in vitro antimicrobial activity of the ligand and metal complexes against bacteria Staphylococcus aureus , B. subtilis, and Escherichia coli, determined by paper disc diffusion method,32 are presented in Table IV, in which the activity of a known antibiotic viz. streptomycin is included for comparison. The results of the in vitro fungicidal activity of the compounds against A. niger and F.oxysporum are given in same table, in which the results of the control are also presented. From Table IV, it is clear that complexes having more antibacterial as well as antifungal activity as compared to free ligands. Although with respect to standard, all the tested compounds were found to be moderately active.

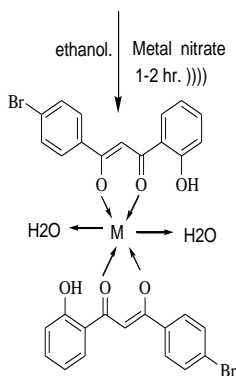**TABLE IV. Antimicrobial activity of the compounds**

Compd .	Conc. (ppm)	Antibacterial activity (inhibition in mm)			Antifungal activity (inhibition in mm)	
		Bacillus subtilis	E. coli	Staphylococcus aureus	Aspergillus. niger	Fusarium oxysporum
$C_{15}H_{11}O_{3}Br$	100	7	7	7	6	7
$C_{32}H_{32}FeBrO_{10}$	100	7	10	7	7	8
$C_{32}H_{32}CoBrO_{10}$	100	11	8	10	7	13
$C_{32}H_{32}NiBrO_{10}$	100	9	8	9	8	17
$C_{32}H_{32}CuBrO_{10}$	100	17	17	18	18	22
$C_{32}H_{32}CrBrO_{10}$	100	15	15	17	16	18
Streptomycin	100	6	7	6	6	6

IV. CONCLUSIONS

Based on the physicochemical and spectral data discussed above, octahedral geometry for Fe(III), Co(II), Ni(II), Cu(II) and Cr(III) complexes are proposed. The ligand and complexes are biologically active and showed enhanced antimicrobial activities compared to standard. A thermal study revealed that the complexes are thermally stable. XRD study suggested the monoclinic crystal system for the Fe(III), Co(II) and Cu(II) complexes.
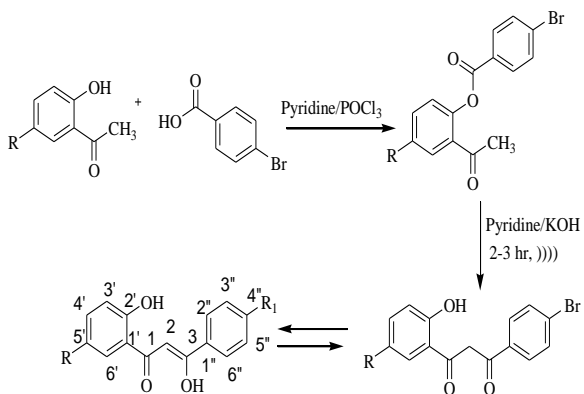
R=H, M= Fe(III), Co(II), Ni(II), Cu(II) and Cr(III)

Scheme 1. Synthesis of ligand and their Metal complexes

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