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Synthesis and studies on Cu(II), Co(II), Ni(II) complexes of Knoevenagel β-diketone ligands

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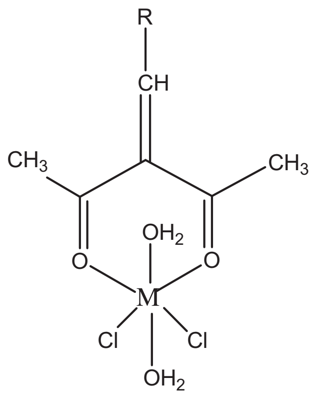
HIGHLIGHTS

- ▶ Planar structure of ligands was confirmed by ^{13}C NMR and IR spectrum.
- ▶ Compare to all the ligand and its metal complexes, ligand **L2** show enhanced activity in both NLO and antimicrobial activity.
- ▶ Ligands and its metal complexes exhibit fluorescence property.
- ▶ The synthesized compounds show strong antimicrobial activity.
- ▶ All the ligands exhibits second harmonic generation (SHG) efficiency.

GRAPHICAL ABSTRACT

Coordination compounds of Cu(II), Co(II), Ni(II) with Knoevenagel β-diketone ligands obtained through the condensation of acetylacetone with different aromatic aldehydes were synthesized and characterized. Fluorescence, second harmonic generation (SHG) efficiency and pharmacological activity of the compounds were tested.



R = (1) $C_6H_4(OH)$ (2) indol-3-yl (3) $C_6H_4(CHO)$

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ABSTRACT

Transition metal complexes of various acetylacetone based ligands of the type ML [where M = Cu(II), Ni(II), Co(II); L = 3-(aryl)-pentane-2,4-dione] have been synthesized. The structural features have been derived from their elemental analysis, magnetic susceptibility, molar conductance, IR, UV–Vis, ^{1}H NMR, Mass and ESR spectral studies. Conductivity measurements reveal that all the complexes are non-electrolytic in nature. Spectroscopic and other analytical data of the complexes suggest octahedral geometry for other metal(II) complexes. The redox behavior of the copper(II) complexes have been studied by cyclic voltammetry. The free ligands and their metal complexes have been screened for their *in vitro* biological activities against the bacteria *Pseudomonas aeruginosa, Escherichia coli* and *Staphylococcus aureus* as well as the fungus *Candida albicans* by well diffusion method. The zone of inhibition value indicates that the most of the metal(II) complexes are found to possess increased activities compared to those of the free ligands. All synthesized compounds may serve as potential photoactive materials as indicated from their characteristic fluorescence properties. The second harmonic generation (SHG) efficiency of the ligands (**L1–L3**) was found to be considerable effect than that of urea and KDP (potassium dihydrogen phosphate).

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Introduction

Metal complexes of β-diketone derivatives have played an important role in coordination chemistry [1–3] and have been widely used in various aspects of industries, such as organic electroluminescent technology, luminescent materials and sensors for bioinorganic applications [4–6]. With an aim to develop novel optical materials, the NLO (nonlinear optical) response of β-diketone, different aromatic aldehydes are introduced in active methylene group by Knoevenagel condensation.

β-Diketone derived complexes show antimicrobial, anti-malarial and antitumorous activities, antioxidant, insecticidal activity. Recently metal(II) complexes have received considerable interest in nucleic acid chemistry because of their chelating nature. The coordination behavior of β-diketones also has significant influences the relative stabilities of the mixed–ligand complexes as well as their use in biomedicine [7–10].

In this connection, our aim is to synthesis Knoevenagel condensate of β-diketone ligands and its metal complexes which have NLO property and pharmacological activities. This present paper reports the spectroscopic characteristics of 3-(aryl)-pentane-2,4-dione (**L1**–**L3**) chelated metal(II) complexes obtained by the condensation of acetylacetone with different substituted aromatic aldehydes and NLO, fluorescence and biological descriptions are presented.

Experimental

Materials

All chemicals and solvents were purchased from commercial sources. Acetylacetone, salicylaldehyde, indole-3-aldehyde and terephaldehyde were Merck India, SD fine products and used as supplied. Solvents were double distilled and stored in molecular sieves (4 Å) before use.

Physical measurements

The UV–Visible spectra of the ligand and their metal complexes were recorded using a JASCO V-530 spectrophotometer. Fluorescence spectra were performed on ELICO SL174 spectrofluorometer using DMF as solvent. The IR spectra in KBr discs were recorded on a SHIMADZU FT-IR 8400 S spectrophotometer. Cyclic voltammetric measurements for Cu(II) complexes in DMSO were performed on a CH Instruments (USA) using a glassy carbon working electrode, platinum wire counter electrode and Ag/AgCl reference electrode. Elemental analyses were performed at SAIF, CDRI-Lucknow. The metal contents of the complexes were estimated by incinerating them to oxides. The chloride ion was estimated by Volhard's method. ^{1}H NMR spectrum was recorded using a Bruker DRX-300 MHz NMR spectrometer. EI mass was recorded by JEOL-GC MATE-2 at IIT, Madras-Chennai. EPR spectrum was recorded by Varian E-112 spectrometer at X-band, using DPPH with 100 kHz modulation frequency and 9.1 GHz microwave frequency at SAIF, IIT Bombay, India. Magnetic susceptibility of the complexes was measured by MSB mark 1 Sherwood U.K. at Thiagarajar College, Madurai. Effective magnetic moments were calculated using the formula $\mu_{\text{eff}} = (2.828\chi_M T)^{1/2}$, where χ_M is the corrected molar susceptibility. The diamagnetic corrections were made by Pascal's constant and Hg[Co(SCN)$_4$] was used as a calibrant. Molar conductance of the complexes (10^{-3} M) was measured in DMF at room temperature using a Systronic conductivity bridge type. The SHG conversion efficiency of the ligands was determined by the modified version of powder technique (IISc, Bangalore).

*Synthesis of 3-(aryl)-pentane-2,4-dione (**L1**–**L3**)(APD)*

The nonenolisable diketone was prepared by employing the modified procedure reported earlier [11]. Acetylacetone (10 g, 10 mmol) was mixed with substituted aromatic aldehyde (10 mmol) and piperidine (1–2 drops) in ethanol (50 ml), and the reaction mixture was stirred thoroughly for a period of 3–6 h with occasional cooling. Gradually a yellow precipitate separated in small amounts. The reaction mixture was set aside to evaporate to dryness and the residual solid was washed with an excess of petroleum-ether to remove any unreacted reagents. Washing was repeated two to three times and the compound was recrystallized from ethanol to give a yellow solid Knoevenagel condensate. The structure of the ligand is shown in Scheme 1.

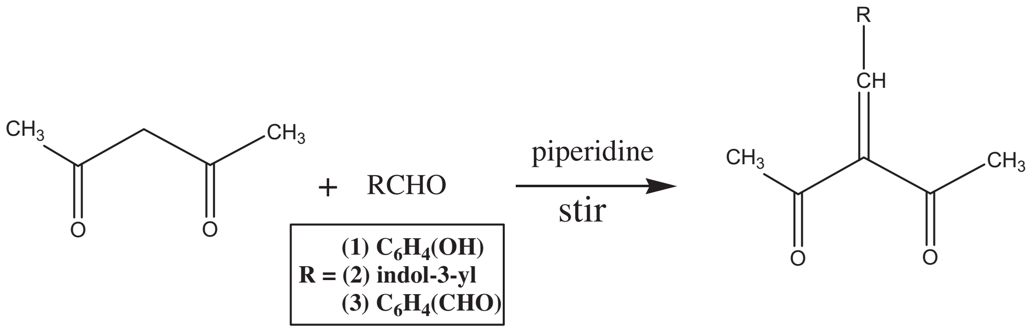
L1. Yield: 85%, m.p.: 98 °C [^{1}H NMR, 6.93–7.50 δ (m, aromatic proton).8.221 δ (s, –C=CH-Ar) [12], 2.66 δ (s, methyl proton) [13], 9.89 δ (s, phenolic –OH); Mass spectra, [M]$^+$ at 204 m/e].

L2. Yield: 58%, m.p.: 125 °C [^{1}H NMR, 7.22–8.10 δ (m, aromatic proton). 8.259 δ (s, –C=CH-Ar), 2.91 δ (s, methyl proton), 9.93 δ (s, =CH–N–), 11.32 δ (s, –NH); Mass spectra, [M]$^+$ at 227 m/e].

L3. Yield: 50%, m.p.: 118 °C [^{1}H NMR, 7.17–7.96 δ (m, aromatic proton). 8.352 δ (s, –C=CH-Ar), 2.33 δ (s, methyl proton), 10.14 δ (s, –CHO); Mass spectra, [M]$^+$ at 216 m/e].

Synthesis of metal(II) complexes

The metal complexes were prepared by the addition of hot solution of the appropriate metal chloride (CuCl$_2$·2H$_2$O, CoCl$_2$·6H$_2$O, NiCl$_2$·6H$_2$O) (10 mmol) in ethanol (25 ml) to the hot solution of the 3-(aryl)-pentane-2,4-dione (10 mmol) in the same solvent (25 ml). The resulting mixture was stirred under reflux for one hour whereupon the complex precipitated. They were collected by filtration, washed thoroughly with ethanol and dried in vacuum.



Scheme 1. Synthesis of ligands (**L1**–**L3**).

*Nonlinear optical properties (NLO) of 3-(aryl)-pentane-2,4-dione (**L1**–**L3**)*

The SHG conversion efficiency of 3-(aryl)-pentane-2,4-dione (**L1**–**L3**) was determined by modified version of powder technique developed by Kurtz and Perry [14]. The compound was ground into powder and packed between two transparent glass slides. A source of Nd:YAG laser beam of wavelength 1064 nm was made to fall normally on the sample cell. The second harmonics signal, generated in the compound was confirmed from the emission of green radiation by the crystal. The SHG radiation of 532 nm green light was collected by a photomultiplier tube (PMT-Philips Photonics-model 8563) after being monochromated (monochromator-model Triax-550) to collect only the 532 nm radiation The efficiency of the sample was compared with microcrystalline powder of KDP and urea. The input energy used in this particular setup was 2.2 mJ/pulse.

Biological activity

The complexes and the ligand were screened for their *in vitro* antibacterial activity against *Pseudomonas aeruginosa* (Gram-negative), *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) and the antifungal activity against *Candida albigans* (Gram-positive). The tests were performed using the disc diffusion method [15] using nutrient broth medium [containing (g/L): beef extract 3 g; peptone 5 g; pH 7.0]. The sterile paper discs (0.5 mm) impregnated with compound dissolved in dimethylsulfoxide (DMSO) at a concentration of 100 μg/mL were used. Then, the paper discs impregnated with the solution of the compound tested were placed on the surface of the media inoculated with the microorganism. The plates were incubated at 35 °C for 24 h. Reading of the results was done by measuring the diameters of the inhibition zones generated by the tested substances using a ruler. Amikacin and ketoconazole were used as positive control for bacteria and fungus respectively.

Result and discussion

The structure of the ligands is also confirmed by NMR, Mass and IR which will be discussed in detailed manner together with its metal complexes later. All the complexes were prepared by direct reaction between ligand and the corresponding metal salts. The analytical data of the ligand and their complexes together with their physical properties are given in Table 1. The complexes are partially soluble in chloroform, acetonitrile but soluble in polar coordinating solvents such as DMF and DMSO. The molar conductance of complexes in 10^{-3} molar DMF solution are in the range 07–16 Ω^{-1} cm^2 mol^{-1} indicating that, these chelates are non electrolytes. The analytical data of the complexes are in good agreement with the general formula $[M(L)X\cdot 2H_2O]$, where M = Cu(II), Ni(II), Co(II); X = $2Cl^-$. The magnetic moment of the complexes is consistent with octahedral geometry around central metal ion for $[M(L)X\cdot 2H_2O]$ (Fig. 1).

Mass spectra

The mass spectra of 3-(aryl)-pentane-2,4-dione and their metal(II) complexes are recorded and shown in supplementary material (Figs. S1–S4). The molecular ion peak for the ligands (**L1**–**L3**) was observed at 204, 227 and 216 m/z. The molecular ion peak is in good agreement with the suggested molecular formula indicated from elemental analyses. The M+/M+2 peak for copper(II) (**L1-Cu(II), L3Cu(II)**) were appeared at 374, 376 and 386, 388 m/z, respectively corresponds to $[MLCl_2\cdot 2H_2O]$. The molecular ion peak is in good agreement with the suggested molecular formula indicated from elemental analyses.

IR spectra

Acetylacetone and its derivative are capable of exhibiting keto-enol tautomerism, but the Knoevenagel condensate of β-diketone with aldehyde produces a non-enolisable product [16]. The IR spectral data of the ligands APD (**L1**–**L3**) and their metal(II) complexes are listed in Table 2. The spectral bands for ligands (**L1**–**L3**) appears in the range of 1633–1699 cm^{-1} and 1614–1583 cm^{-1} are assigned to the stretching vibrations of $\nu(C{=}O)$ and $\nu(C{=}C)$ [17,18] respectively. The shifting of the same bands to lower frequency in all the metal(II) complexes implies the coordination of carbonyl group to the central metal ion. The band at around 3400 cm^{-1} for the complexes ascertains the existence of

Table 1
Elemental analysis, molar conductance and magnetic susceptibility data of ligands (**L1**–**L3**) and their metal(II) complexes.

Compound	Formula weight (g mol^{-1})	m.p. (°C)	Calculated (Found), %				Λ_M (Ω^{-1} cm^2 M^{-1})	μ_{eff} (BM)
			M	C	H	Cl		
$[C_{12}H_{12}O_3]$ **L1**	204	98–100	–	70.6 (70.2)	5.88 (5.86)	–	–	–
$[CuL1Cl_2\cdot 2H_2O]$**L1Cu**(**II**)	373	133–135	16.8 (16.4)	38.5 (38.3)	3.20 (3.18)	18.7 (18.6)	14	1.89
$[CoL1Cl_2\cdot 2H_2O]$ **L1Co**(**II**) (16.4)	369 (38.5)	142–145 (3.20)	16.6 (18.6)	38.9	3.22	18.9	8	4.75
$[NiL1Cl_2\cdot 2H_2O]$ **L1Ni**(**II**)	368	148–150	16.5 (16.3)	38.8 (38.5)	3.30 (3.28)	19.0 (18.8)	13	3.28
$[C_{14}H_{13}NO_2]$ **L2**	227	125–127	–	74.0 (74.8)	5.70 (5.66)	–	–	–
$[CuL2Cl_2\cdot 2H_2O]$ **L2Cu**(**II**)	396	143–145	15.8 (15.6)	42.3 (42.0)	4.20 (4.15)	17.6 (17.4)	10	1.93
$[CoL2Cl_2\cdot 2H_2O]$ **L2Co**(**II**)	392	158–159	14.9 (14.6)	42.8 (42.7)	4.33 (4.30)	17.8 (17.5)	15	4.82
$[NiL2Cl_2\cdot 2H_2O]$ **L1Ni**(**II**)	391	166–168	14.8 (14.4)	42.7 (42.5)	4.31 (4.29)	17.9 (17.5)	9	3.31
$[C_{13}H_{12}O_3]$ **L3**	216	118–120	–	72.2 (72.0)	5.55 (5.52)	–	–	–
$[CuL3Cl_2\cdot 2H_2O]$ **L3Cu**(**II**)	385	135–137	16.3 (16.1)	40.4 (40.0)	4.14 (4.12)	18.1 (17.8)	14	1.95
$[CoL3Cl_2\cdot 2H_2O]$ **L3Co**(**II**)	381	148–149	15.4 (15.3)	40.8 (40.5)	4.45 (4.43)	18.3 (18.0)	16	4.78
$[NiL3Cl_2\cdot 2H_2O]$ **L3Ni**(**II**)	380	152–154	15.3 (15.2)	40.7 (40.5)	4.45 (4.43)	18.4 (18.2)	7	3.26

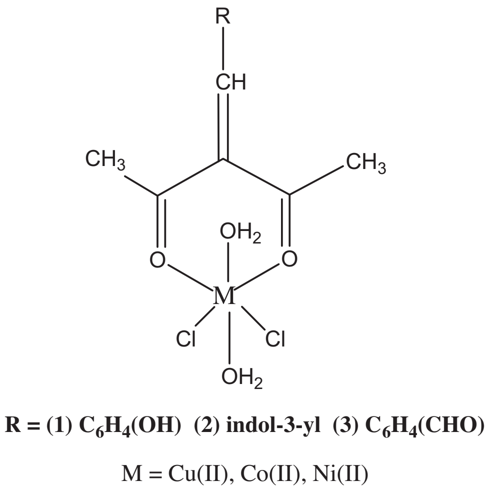


Fig. 1. Proposed structure of metal(II) complexes.

Table 2
Characteristic infrared vibrational frequencies (cm^{-1}) for **L1**–**L3** ligands and their metal(II) complexes.

Compound	ν(C=O)	ν(C=C)	ν(OH) of H_2O
L1	1688	1614	–
L1Cu(II)	1658	1601	3448
L1Co(II)	1666	1573	3459
L1Ni(II)	1666	1575	3449
L2	1633	1583	–
L2Cu(II)	1626	1514	3462
L2Co(II)	1629	1516	3390
L2Ni(II)	1625	1517	3477
L3	1699	1610	–
L3Cu(II)	1689	1586	3431
L3Co(II)	1691	1580	3442
L3Ni(II)	1691	1583	3458

coordinated water in all the complexes. The new band appeared in the 520–545 cm^{-1} region in the case of complexes are assigned to ν(M–O) [19].

Electronic spectra

The electronic absorption spectral data (cm^{-1}) of the metal(II) complexes are given in Table 3. The Cu(II) complexes (**L1Cu**(**II**)–**L3Cu**(**II**)) under the present investigation display two to three absorption bands at 22,831–23,923 cm^{-1}, 22,522–22,883 cm^{-1} and 9460–12,515 cm^{-1}, which are assigned as an intraligand charge transfer (INCT) band, ligand-to-metal charge transfer band and ${}^2E_g \to {}^2T_{2g}$ transitions [17], respectively. Their μ_{eff} values of 1.84–1.95 BM supportive of octahedral geometry around Cu(II) [20]. Their molar extinction coefficient (ε) varies to several hundred M^{-1} cm^{-1} supporting again the non centro symmetric nature of the complex [21].

In the present electronic absorption spectrum of all the Co(II) complexes (**L1Co**(**II**)–**L3Co**(**II**)), exhibit three d-d bands at 9541–9900 cm^{-1}, 16,420–16,501 cm^{-1} and 19,047–20,576 cm^{-1} assignable to ${}^4T_{1g}$ (F)→4T_{2g} (F), ${}^4T_{1g} \to {}^4A_{2g}$ and ${}^4T_{1g}$ (F)→${}^4T_{1g}$ (P) transitions [22] respectively, and the magnetic moments for the cobalt(II) complexes in the 4.71–4.82 BM range supporting octahedral geometry [23]. The molar absorptivities of the bands are in the range of hundreds indicating geometry of the complexes.

All the Ni(II) complexes (**L1Ni**(**II**)–**L3**(**Ni**(**II**)) in this paper show bands at 9541–10,582 cm^{-1}, 14,471–16,420 cm^{-1} and 20,576–25,038 cm^{-1} due to ${}^3A_{2g} \to {}^3T_{2g}$, ${}^3A_{2g} \to {}^3T_{1g}$ (F) and ${}^3A_{2g} \to {}^3T_{1g}$ (P) transitions [24] respectively with comparatively low intensities (ε). The magnetic moments value of above Ni(II) complexes fall the range of 3.21–3.31 BM range normally observed for octahedral coordination geometry [25].

The ligand field splitting energy (10Dq), interelectronic repulsion parameter (B) and covalency factor (nephelauxetic ratio) (β) for the octahedral Co(II) and Ni(II) complexes have been calculated using the secular equation given by Konig [26].

For Co(II) complexes	For Ni(II) complexes
$10Dq = 1/2[(2\nu_1 - \nu_3) + (\nu_3^2 + \nu_1\nu_3 - \nu_1^2)^{1/2}]$	$10Dq = \nu_1$
$15B = \nu_3 - 2\nu_1 + 10Dq$	
$15B = (\nu_2 + \nu_3) - 3\nu_1$	$\beta = B/B_0$ [B_0 (free ion) = 971]
$\beta = B/B_0$ [B_0 (free ion) = 1030]	
$\beta_0 = (1 - \beta) \times 100$	
$\beta_0 = (1 - \beta) \times 100$	

The calculated values of ligand field splitting energy (10Dq), the Racah interelectronic repulsion parameter (B), the nephelauxetic ratio (β), and the ratio ν_2/ν_1 (Table 4) support the proposed geometry for all the synthesized Ni(II) and Co(II) octahedral complexes. The nephelauxetic ratio (β) for the Co(II) and Ni(II) complexes is less than one suggesting partial covalency in the metal ligand bond. The octahedral geometry of these complexes is further supported by the value of ν_2/ν_1. In general, sterically bulky ligands give rise to relatively low Dq values [21]. Here, the value of 10Dq obtained in the case of 3-((1H-indol-3-yl)methylene)pentane-2,4-dione (**L2**) metal complex is relatively low which clearly show the considerable amount of bulkiness in the complex.

Electrochemical behavior

The redox behavior of Cu(II) complexes has been investigated by cyclic voltammetry (Table 5). The cyclic voltammograms of the copper(II) complexes recorded at room temperature using TBAP (tetrabutylammoniumperchlorate) as the supporting electrolyte in the potential range 1.2 to −1.2 V reveal that the peak current for the copper(II) complexes varies with the change of Knoevenagel condensate of 3-(aryl)-pentane-2,4-dione. The free ligand does not show oxidation or reduction peaks. The cathodic current function values of copper complex were found to be independent of the scan rate. The repeated scans as well as different scan rates show that dissociation does not take place in the complex. The $E_{pa} - E_{pc}$ values are greater than 200 mV, which indicates that the reduction processes are irreversible [27] in nature and the ratio of anodic to cathodic peak currents corresponding to the chemical change occurs with the electron transfer as Cu(II)→Cu(I)→Cu(0) (Fig. S5).

EPR spectra

The EPR spectra of copper(II) complexes were recorded in DMSO at 300 and 77 K and the spin Hamiltonian parameters of the complexes are listed in Table 6. The observed spectral parameters show that the $g_{||} > g_{\perp}$ value is characteristic of an axially elongated octahedral geometry [28]. The covalent character of metal-ligand bond is inferred from the g_{iso} value 2.28–2.60, it also support the fact that the unpaired electrons lies predominantly in the

Table 3
Electronic spectral data (cm^{-1}) (ε) of metal(II) complexes.

Complexes	Frequency (ε, M^{-1} cm^{-1})	Assignment	Geometry
L1Cu(II)	23,923 (492)	INCT	
	22,883 (425)	INCT	Distorted octahedral
	12,515 (151)	$^2E_g \rightarrow ^2T_{2g}$	
L1Co(II)	9689 (38)	$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$	
	6420 (59)	$^4T_{1g} \rightarrow ^4A_{2g}$	Distorted octahedral
	19,267 (290)	$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$	
L1Ni(II)	9680 (55)	$^3A_{2g} \rightarrow ^3T_{2g}$	
	14,534 (395)	$^3A_{2g} \rightarrow ^3T_{1g}(F)$	Distorted octahedral
	21,097 (453)	$^3A_{2g} \rightarrow ^3T_{1g}$ (P)	
L2Cu(II)	23,148 (164)	INCT	Distorted octahedral
	10,695 (60)	$^2E_g \rightarrow ^2T_{2g}$	
L2Co(II)	9541 (259)	$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$	
	16,420 (952)	$^4T_{1g} \rightarrow ^4A_{2g}$	Distorted octahedral
	20,576 (920)	$^4T_{1g}$ (F)$\rightarrow ^4T_{1g}$ (P)	
L2Ni(II)	9541 (389)	$^3A_{2g} \rightarrow ^3T_{2g}$	
	14,771 (652)	$^3A_{2g} \rightarrow ^3T_{1g}$ (F)	Distorted octahedral
	20,956 (915)	$^3A_{2g} \rightarrow ^3T_{1g}$ (P)	
L3Cu(II)	22,831 (280)	INCT	Distorted octahedral
	10,964 (150)	$^2E_g \rightarrow ^2T_{2g}$	
L3Co(II)	9680 (50)	$^4T_{1g}$ (F)$\rightarrow ^4T_{2g}$ (F)	
	16,447 (175)	$^4T_{1g} \rightarrow ^4A_{2g}$	Distorted octahedral
	19,047 (154)	$^4T_{1g}$ (F)$\rightarrow ^4T_{1g}$ (P)	
L3Ni(II)	10,010 (255)	$^3A_{2g} \rightarrow ^3T_{2g}$	
	14,471 (475)	$^3A_{2g} \rightarrow ^3T_{1g}$ (F)	Distorted octahedral
	23,198 (1411)	$^3A_{2g} \rightarrow ^3T_{1g}$ (P)	

INCT – intraligand charge transition; solvent – DMSO; concentration in 10^{-3} mol/L.

Table 4
Electronic parameters of metal(II) complexes (**L1**–**L3**).

Compounds	v_2/v_1	B (cm^{-1})	β	β_o	10Dq (cm^{-1})
$[Co(L1)Cl_2(H_2O)_2]$	1.69	714	0.73	27	10,826
$[Ni(L1)Cl_2(H_2O)_2]$	1.50	439	0.43	57	9680
$[Co(L2)Cl_2(H_2O)_2]$	1.72	816	0.84	16	10,749
$[Ni(L2)Cl_2(H_2O)_2]$	1.51	473	0.46	54	9541
$[Co(L3)Cl_2(H_2O)_2]$	1.69	699	0.72	28	10,803
$[Ni(L3)Cl_2(H_2O)_2]$	1.51	509	0.49	51	10,010

Table 5
Redox potential for copper(II) complexes.

Complexes	Epc (V)	Epa (V)	ΔEp (V)
L1Cu(II)	0.120	0.590	0.470
L2Cu(II)	0.140	0.370	0.230
L3Cu(II)	0.075	0.762	0.687

Table 6
The spin Hamiltonian parameters of copper(II) complexes.

Copper(II) complex	A_{iso}	g_{iso}	$g_{\|\|}$	$g_{\perp}$	$A_{\|\|}$	$A_{\perp}$	α^2	β^2	$g_{\|\|}/A_{\|\|}$ (cm)
	(10^{-4} cm^{-1})				(10^{-4} cm^{-1})				
L1Cu(II)	122	2.31	2.29	2.14	128.7	122.1	0.36	2.91	177
L2Cu(II)	112	2.60	2.59	2.05	175.0	121.2	0.56	3.66	148
L3Cu(II)	113	2.28	2.35	2.21	149.9	59.5	0.42	2.90	157

$d_{x^2-y^2}$ orbital. The G values for copper(II) complexes lies in the range 1.96–3.94 and for **L2Cu(II)** complex G value greater than 4 suggest that the local tetragonal axes are aligned parallel or slightly misaligned and consistent with a $d_{x^2-y^2}$ ground state. For the other copper(II) complexes the G value is less than 4 which indicates that the exchange coupling interaction is considerable and misalignment is appreciable. The calculated magnetic moment for the copper(II) complexes (1.84–1.90 BM) using the relation $\mu^2 = 3/4\,|g|^2$ and is indicative of an unpaired electron. The α^2 values suggest appreciable in-plane covalency in the molecule. The calculated value of ($g_{||}/A_{||}$) for the complexes is characteristic of distorted structure. The poor in-plane π bonding in the complex is reflected in their β^2 values. The molecular orbital coefficients α^2, β^2 were calculated using the following equations (Figs. S6–S8).

$$\alpha^2_{Cu} = A_{\|}/p + (g_{\|} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

$$\beta^2_{Cu} = (g_{\|} - 2.0023)E/(-8\lambda\alpha^2)$$

Fluorescence study

The fluorescent nature of 3-(aryl)-pentane-2,4-dione (**L1**–**L3**) and their metal(II) complexes are shown in Table 7. Ligands have been inferred from their emission bands around 354–541 nm. The metal(II) complexes of all the above ligands also exhibit three emission bands in the range of 486–797 nm. Significant differences in the positions of emissions maximum of 3-(aryl)-pentane-2,4-dione and its complexes establish the complexation process [29]. All the complexes register broad emission bands indicating charge transfer nature of the transitions. Quenching of fluorescence of ligand by transition metal ions during complexation is a rather common phenomenon which is explained by processes such as redox-activity, electronic energy transfer [30]. The free ligand shows an enhanced fluorescent intensity. This emission is neither MLCT nor LMCT in nature. It is known that lone pair of electron on oxygen and on carbonyl chromophore can quench the fluorescence of aromatic system through photo induced electron transfer. This leads to draining out of these pairs of electrons on to the metal orbital via complex formation which causes a suppression of this fluorescence intensity [31] (Figs. S9 and S10).

NLO property of 3-(aryl)-pentane-2,4-dione

The SHG (second harmonic generation) efficiency of the different acetylacetone based Knoevenagel condensates are presented in Table 8. On Comparing the SHG efficiency of the ligands (**L1**–**L3**), the 3-((1H-indol-3-yl)methylene)pentane-2,4-dione (**L2**) shows much higher efficiency than others. This may be due to the presence of indole nucleus. In general molecule with delocalized π-electron system can have large nonlinear polarizabilities [32] and it has been generally understood that the molecular nonlinearity can be enhanced by systems with strong donor and acceptor groups [33]. From the analysis of electronic transitions and molecular orbital involved, ligand orbital can improve the NLO properties. The attempt to study the NLO efficiency of metal(II) complexes of 3-(aryl)-pentane-2,4-dione (**L1**–**L3**) are much lower than the references (KDP and urea).

Biological activity

Zone of inhibition values of the investigated compounds against the *bacteria and fungus* are summarized in Table 9. The observed values indicate that 3-((1H-indol-3-yl)methylene)pentane-2,4-

Table 7
Fluorescence parameters of ligand (**L1**–**L3**) and its metal(II) complexes in DMSO.

Compound	Emission maximum (nm)		
	L1	**L2**	**L3**
Ligand (**L**)	439, 541	354, 427	411, 510
Cu(II) complex	591,768,785	517,793,800	545,789,796
Co(II) complex	621,698,783	520,784,795	498,788,797
Ni(II) complex	578,789,792	681,783,794	669,778,793

Table 8
SHG parameters of different knoevenagel condensate of 3-(aryl)-pentane-2,4-dione.

Compound	SHG efficiency with respect to KDP	SHG efficiency with respect to urea
L1	0.4	0.09
L2	4.6	1.05
L3	0.5	0.11

Table 9
Anti microbial activity of the ligands (**L1**–**L3**) and their metal(II) complexes (zone of inhibition in mm[a]; concentration in 10^{-3} mol/L).

Compound	*P. aeruginosa*			*S. aureus*			*E. coli*			*C. albicans*		
	L1	**L2**	**L3**	**L1**	**L2**	**L3**	**L1**	**L2**	**L3**	**L1**	**L2**	**L3**
Ligand (**L**)	9	13	12	9	12	8	6	11	10	7	9	8
Cu(II) complex	17	14	R	15	11	R	6	R	R	8	R	R
Co(II) complex	16	16	14	10	14	9	8	15	17	9	13	14
Ni(II) complex	14	18	16	13	12	R	9	13	16	R	10	13
Amikacin	18			18			18			–		
Ketoconazole	–			–			–			12		
DMSO	–			–			–			–		

Limits values for bacterial/fungus activity zones: weak = up to 6 (up to 4); medium = 7–12 (5–8); strong = 13–18 (9–12). R = resistance.

[a] Each value observed is within the error limits of ±1.

dione (**L2**) has higher activity than other ligands and similarly, most of the complexes have higher activity than the free ligand. Such an increased activity of the ligand may be due to the presence of indole nucleus and in complexes it can be explained on the bases of chelation theory [34]. On chelation, polarity of the metal ion is reduced to a greater extent due the overlapping of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Moreover, delocalization of the π-electrons over the whole chelate ring is increased and lipophilicity of the complexes is enhanced. The increased lipophilicity enhances the penetration of the complexes into the lipid membranes and blocks the metal binding sites in the enzymes of microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism. Investigation on similar type of complexes [35–37] reveals that metal complexes exhibit higher activity than their ligand. The compounds of our interest also exhibit higher activity than respective ligands, but in no case it is effective towards their standard drug.

Conclusion

Knoevenagel condensate of 3-(aryl)-pentane-2,4-dione (**L1**–**L3**) has been synthesized from acetylacetone and various substituted aromatic aldehydes and their metal complexes [$MLCl_2$] for M: L ratio 1:1 of Cu(II), Co(II), Ni(II) were obtained. An octahedral structure has been proposed for all the metal(II) complexes. Though some Knoevenagel condensed complexes have been found in recent literature, these have been rarely seen as nonlinear optical material in terms of second harmonic generation (SHG) efficiency. In our system all the ligands (**L1**–**L3**) of Knoevenagel condensate found to exhibit considerable nonlinear optical (NLO) property in comparison with urea and KDP. All the ligands and its metal(II) complexes are fluorescent in nature. Metal(II) complexes exhibited a considerable antimicrobial activity compared to the free ligands.

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Appendix Supplementary. data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.06.018.

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