

Research Article

Spectral, NLO, Fluorescence, and Biological Activity of Knoevenagel Condensate of β -Diketone Ligands and Their Metal(II) Complexes

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Transition metal complexes of various acetylacetonate-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, ¹H NMR, mass and ESR spectral studies. Conductivity measurements reveal that all the complexes are nonelectrolytic in nature. Spectroscopic and other analytical data of the complexes suggest square planar geometry for copper(II), cobalt(II), and nickel(II) complexes of 3-(3-phenylallylidene)pentane-2,4-dione and octahedral geometry for other metal(II) complexes. The redox behaviors 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 *bacteria* and *fungus*. 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 was found to have considerable effect compared to that of urea and KDP.

1. 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]. β -diketone derivatives possess a broad spectrum of biological effects such as anti-inflammatory and antimicrobial activity effects [2–6].

Nonlinear optics has received considerable attention due to its variety of applications in optoelectronic and photonic devices. A wide variety of materials have been investigated for NLO, among which both organic and inorganic materials are attractive because of their optical and electronic properties which can be tailored by structural modification [7–11]. There is a need to design and develop the nonlinear optical materials to meet the present demand due to their widespread applications such as high-speed information processing, optical communications, and optical data storage [12, 13]. With an aim to develop novel optical materials, in recent years, some NLO response compounds [14, 15]

were designed and prepared by our group. In an attempt to increase the NLO response of β -diketone, here different aromatic aldehydes were introduced in active methylene group.

In this connection, our aim is to synthesize the ligands which have NLO property and pharmacological activities. This paper reports the spectroscopic characteristics of 3-(aryl)-pentane-2,4-dione-chelated metal(II) complexes prepared by the condensation of acetylacetonate with different substituted aromatic aldehydes, and NLO, fluorescence, and biological descriptions are presented.

2. Experimental

All chemicals and solvents were purchased from commercial sources. Acetylacetonate, benzaldehyde, and cinnamaldehyde were Merck India, SD fine products and used as supplied. Solvents were double distilled and stored in molecular sieves (4 Å) before use. For voltammetric experiments, tetrabutylammonium perchlorate (TBAP) (Sigma) was used

as supporting electrolyte. NMR measurement was made on a BRUKER 300 MHz spectrometer. The UV-Vis spectra were recorded on a THERMO SPECTRONIC 6 HEXIOS α , and fluorescence spectra were performed on ELICO SL174 spectrofluorometer using DMSO as solvent. EI mass was recorded by GEOL-GC MATE-2 mass spectrometer. The IR spectra were carried out by using SHIMADZU FTIR 8400 spectrophotometer. ESR spectra of the copper(II) complexes were obtained at 300 and 77 K using DPPH (diphenylpicrylhydrazide) as the g-marker. Magnetic susceptibility of the complexes was measured on a Sherwood Magnetic susceptibility balance Mk1. Cyclic voltammetric studies for Cu(II) complexes in DMSO were taken on a CH Instruments (USA). Molar conductance of the complexes was measured in DMSO at room temperature using Systronic Conductivity Bridge 304. All the complexes were screened for biological activity through well diffusion method.

2.1. Synthesis of 3-(Aryl)-pentane-2,4-dione (L1, L2). The nonenolisable diketone was prepared by employing the modified procedure reported earlier [16]. Acetylacetone (3 g, 1 mmol) was mixed with substituted aromatic aldehydes (1 mmol) (benzaldehyde (3.1 g, 1 mmol) and cinnamaldehyde (3.9 g, 1 mmol), resp., for L1 and L2), and piperidine (0.05 cm³) in ethanol (50 mL), and the reaction mixture was stirred thoroughly for a period of 6 h with occasional cooling. Gradually a yellow precipitate was 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 (see Supplementary Figures 3 and 4 in Supplementary Material available online at doi:10.1155/2011/154326).

L1-Yield: 80%, m.p: 132°C [¹H NMR, 7.11–7.40 δ (m, aromatic proton). 8.229 δ (s, –C=CH–Ar) [17], 2.09 δ (s, methyl proton) [18]; ¹³C NMR, 8 peaks corresponding to the carbon atom; Mass spectra, [M]⁺ at 188 m/e].

L2-Yield: 70%, m.p: 126°C [¹H NMR, 7.23–7.90 δ (m, aromatic proton). 8.251 δ (s, –C=CH–Ar), 2.69 δ (s, methyl proton), 6.68 δ (t, –CH=CH); ¹³C NMR, 10 peaks corresponding to the carbon atom; Mass spectra, [M]⁺ at 214 m/e].

2.2. Synthesis of Metal(II) Complexes. The metal complexes were prepared by the addition of hot solution of the appropriate metal chloride (1 mmol) in ethanol (25 mL) to the hot solution of the 3-(aryl)-pentane-2,4-dione (1 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.

2.3. Nonlinear Optical Properties (NLO) of 3-(Aryl)-pentane-2,4-dione (L1, L2). The SHG conversion efficiency of 3-(aryl)-pentane-2,4-dione (L1, L2) was determined by modified version of powder technique developed by Kurtz and

Perry [19]. The ligands were ground into powder and packed between two transparent glass slides. An Nd:YAG laser beam of wavelength 1064 nm was made to fall normally on the sample cell. The transmitted fundamental wave absorbed by a CuSO₄ solution removes the incident 1064 nm light, and Filter BG-38 also removes any residual 1064 nm light. Interference filter band width is 4 nm and of central wavelength 532 nm. The green light is finally detected by the photomultiplier tube and displayed on the oscilloscope. The second harmonic signal was detected by a photomultiplier tube and displayed on a storage oscilloscope. The efficiency of the sample was compared with that of microcrystalline powder of KDP and urea. The input energy used in this particular setup is 2.2 mJ/pulse.

2.4. Biological Activity. Antimicrobial activity of the compounds was tested *in vitro* by the well diffusion method [20] against the bacteria *Pseudomonas aeruginosa*, *Escherichia coli*, and *Staphylococcus aureus* using agar nutrient as the medium. Also the antifungal activity against the fungus *Candida albicans* cultured on potato dextrose using agar as medium was tested. About 0.5 mL spore suspension of each investigated organism was added to a sterile Petri dish and left to solidify, and the well was made in each plate with the help of a cork-borer (6 mm). The stock solution (10⁻³ mol/L) was prepared by dissolving the compounds in DMSO. The plates were inoculated with microorganisms and filled with the test solution for 24 h for bacteria and 48 h for fungus at 37°C. The activity was measured in terms of zone of inhibition against bacteria and fungus appearing around the well.

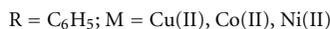
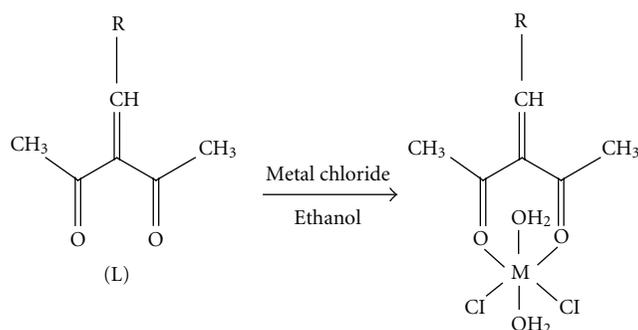
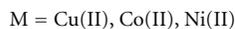
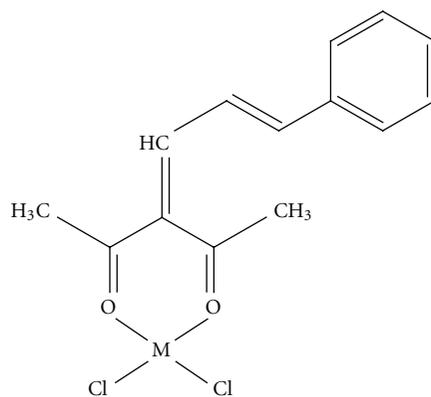
3. Result and Discussion

The analytical data and physical properties of the 3-(aryl)-pentane-2,4-dione (**L1** and **L2**) and metal(II) complexes are presented in Table 1. The molar conductance of the complexes implies that all the complexes are not electrolytes. The analytical data of the complexes are in good agreement with the general formula [M(L1)X·2H₂O], where M = Cu(II), Ni(II), Co(II); X = 2Cl⁻ except copper(II), cobalt(II), and nickel(II) complexes of 3-(3-phenylallylidene)pentane-2,4-dione, which is of [M(L2)X] type. The magnetic moment of the complexes is consistent with octahedral and square planar geometry around central metal ion for [M(L1)X·2H₂O] and [M(L2)X] types, respectively (Figures 1 and 2).

3.1. Mass Spectra. In the mass spectrum of 3-(aryl)-pentane-2,4-dione and metal(II) complexes, the molecular ion peaks for the ligands **L1** and **L2** were observed at 188 and 214 m/z, whereas the M+/M+2 peak for nickel(II) (**L1c**) was observed at 353, 355 corresponds to [MLCl₂·2H₂O]. Similarly, cobalt(II) complex of 3-(3-phenylallylidene)pentane-2,4-dione (**L2b**) exhibits the molecular ion and M+2 peak at 342, 344 m/z corresponds to [MLCl₂]. Peak at 355 and 344 m/z in L1c and L2b, respectively, corresponds to isotopic peak which also confirms the presence of chlorine ion in the complexes (Supplementary Figures 5 and 6).

TABLE 1: Elemental analysis, molar conductance, and magnetic susceptibility data of ligands **L1** and **L2** and their metal(II) complexes.

Compound	m.p (°C)	Calculated (Found), %			Λ_M (S cm ² M ⁻¹)	μ_{eff} (BM)
		M	C	H		
L1	132	—	76.5 (76.4)	6.38 (6.36)	—	—
[CuL1Cl ₂ ·2H ₂ O] L1a	160–162	17.6 (17.4)	40.2 (40.0)	3.35 (3.31)	10	1.95
[CoL1Cl ₂ ·2H ₂ O] L1b	154–157	16.5 (16.4)	40.7 (40.2)	3.39 (3.35)	9	4.71
[NiL1Cl ₂ ·2H ₂ O] L1c	171–172	16.4 (16.2)	40.5 (40.0)	3.38 (3.35)	15	3.21
L2	126	—	78.5 (78.3)	6.54 (6.50)	—	—
[CuL ₂ Cl ₂] L2a	156–158	16.4 (16.1)	43.7 (43.5)	4.68 (4.66)	18	1.79
[CoL ₂ Cl ₂] L2b	149–151	17.1 (16.8)	48.9 (48.6)	4.07 (4.05)	14	1.85
[NiL ₂ Cl ₂] L2c	163–165	17.0 (16.7)	48.8 (48.4)	4.05 (4.03)	12	—

FIGURE 1: Synthesis of metal(II) complexes (**L1a**, **L1b**, **L1c**).FIGURE 2: The proposed structure of metal(II) complexes (**L2a**, **L2b**, and **L2c**).

3.2. *IR Spectra.* Acetylacetone and its derivative are capable of exhibiting keto-enol tautomerism, but the Knoevenagel condensate of β -diketone with aldehyde produces a nonenolizable product [21]. The IR spectral data of the ligands (**L1** and **L2**) and their metal(II) complexes are listed in Table 2. The spectral bands for ligands (**L1** and **L2**) appears in the range of 1695, 1699 cm⁻¹ and 1600, 1629 cm⁻¹ are

assigned to the stretching vibrations of $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ [22, 23] 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 coordinated water in all the complexes except copper(II), cobalt(II), and nickel(II) of **L2**. The new

TABLE 2: IR spectral data (cm^{-1}) of ligands **L1** and **L2** and their metal(II) complexes.

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{OH})$ of H_2O
L1	1695	1600	—
L1a	1676	1548	3448
L1b	1629	1540	3427
L1c	1683	1563	3419
L2	1699	1629	—
L2a	1651	1597	—
L2b	1687	1614	—
L2c	1685	1620	—

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

Complexes	Frequency (ϵ)	Assignment	Geometry
L1a	23148 (3015)	INCT	Distorted octahedral
	21097 (2131)	INCT	
	9460 (856)	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$	
L1b	9541 (350)	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$	Distorted octahedral
	16420 (760)	${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$	
	19047 (1289)	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	
L1c	10582 (410)	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$	Distorted octahedral
	14471 (997)	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$	
	25038 (1425)	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$	
L2a	23529 (1895)	INCT	Square planar
	18867 (530)	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$	
L2b	16474 (285)	${}^2\text{B}_2 \rightarrow {}^2\text{E}_g$	Square planar
	21852 (355)	${}^4\text{A}_{1g} \rightarrow {}^4\text{B}_{1g}$	
L2c	15337 (543)	${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$	Square planar
	21582 (1564)	${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$	

band that appeared in the $520\text{--}532\text{ cm}^{-1}$ region in the case of complexes is assigned to $\nu(\text{M}-\text{O})$ [24] (Supplementary Figures 7 and 8).

3.3. Electronic Spectra. The electronic absorption spectral data (cm^{-1}) of the metal(II) complexes are given in Table 3. Copper(II) complex (**L1a**) displays three absorption bands at 23148 cm^{-1} , 21097 cm^{-1} and 9460 cm^{-1} , which are assigned as an intraligand charge transfer (INCT) band [25], ligand-to-metal charge transfer band, and ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transitions, [22] respectively. Their μ_{eff} values of 1.95 BM are supportive of octahedral geometry around Cu(II) [26]. Co(II) complex (**L1b**) exhibits three d-d bands at 9541 cm^{-1} , 16420 cm^{-1} and 19047 cm^{-1} assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$, and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions [27], respectively, and the magnetic moments for the cobalt(II) complexes in the 4.71 BM range are supportive of octahedral geometry [28]. Similarly, Ni(II) complex (**L1c**) shows bands at 10582 cm^{-1} , 14471 cm^{-1} and 25038 cm^{-1} due to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$, and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions [29], respectively. The magnetic moment values of the above Ni(II) complexes fall in the range of 3.21 BM, which is in the normal range observed for octahedral Ni(II) complexes ($\mu_{\text{eff}} = 2.9\text{--}3.3\text{ BM}$) [26, 30]. This indicates that the complex

of Ni(II) is six-coordinate and probably octahedral geometry [31].

The electronic spectrum of the present 3-(3-phenylallylidene)pentane-2,4-dione copper(II) complex (**L2a**) showed absorption band at 18867 cm^{-1} (530 nm) assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transition, which corresponds to a square planar geometry around Cu(II) ion [32]. The absence of absorption below 10000 cm^{-1} excludes the possibility of tetrahedral geometry for the complexes. Additional band at 23529 cm^{-1} (425 nm) attributed to INCT may also in the spectra of square planar complexes [33]. The magnetic moment of the copper(II) complex is 1.79 BM and is also supportive of square planar geometry.

In the electronic spectrum of cobalt(II) (**L2b**) complex the bands at 16474 cm^{-1} and 21852 cm^{-1} are assigned to ${}^2\text{B}_2 \rightarrow {}^2\text{E}_g$ and ${}^4\text{A}_{1g} \rightarrow {}^4\text{B}_{1g}$ transitions [34], respectively, characteristic of square planar geometry, and the same is further evidenced by its magnetic moment value 1.85 BM [35]. Similarly, in the UV spectrum of nickel(II) (**L2c**) complex the bands at 15337 cm^{-1} and 21582 cm^{-1} arising from ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$, and ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ transitions, respectively [36], and its magnetic moment value also confirm square planar geometry [37].

TABLE 4: Redox potential for copper(II) complexes.

Complexes	E_{pc} (V)	E_{pa} (V)	ΔE_p (V)
L1a	0.062	0.780	0.712
L2a	0.102	0.766	0.765

TABLE 5: The spin Hamiltonian parameters of copper(II) complexes.

Copper(II) complex	A_{iso} (10^{-4} cm $^{-1}$)	g_{iso}	g_{\parallel}	g_{\perp}	A_{\parallel} (10^{-4} cm $^{-1}$)	A_{\perp}	α^2	β^2	$g_{\parallel}/A_{\parallel}$ (cm)
L1a	121	2.29	2.28	2.06	122.3	116.2	0.34	2.98	186
L2a	180	2.32	2.29	2.15	122.1	115.9	0.33	2.70	176

TABLE 6: Fluorescence parameters of ligands **L1** and **L2** and their metal(II) complexes in DMSO.

Compound	Emission maximum (nm)	
	L1	L2
Ligand (L)	498.5	379
a -Cu(II) complex	578, 789, 792	595, 684, 784
b -Co(II) complex	500, 789, 793	486, 785, 793
c -Ni(II) complex	677, 787, 795	660, 784, 796

3.4. Electrochemical Behavior. The cyclic voltammograms (Table 4) of the copper(II) complexes recorded at room temperature using TBAP 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 $E_{pa} - E_{pc}$ values are greater than 200 mV, which indicates that the reduction processes are irreversible [38] in nature and the ratio of anodic to cathodic peak currents corresponding to the chemical change occurs with the electron transfer as $Cu(II) \rightarrow Cu(I) \rightarrow Cu(0)$.

3.5. 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 5. The observed spectral parameters show that the $g_{\parallel} > g_{\perp}$ value is characteristic of an axially elongated octahedral geometry [37]. The covalent character of metal-ligand bond is inferred from the g_{iso} values 2.29 and 2.32, and it also supports the fact that the unpaired electrons lie predominantly in the $d_{x^2-y^2}$ orbital. The G values for the copper(II) (**L1a**) complex greater than 4 suggest that the local tetragonal axes are aligned parallel or slightly misaligned and are consistent with a $d_{x^2-y^2}$ ground state. For the other copper(II) complex (**L2a**) 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 using the relation $\mu^2 = 3/4|g|^2$ is indicative of an unpaired electron. The α^2 values suggest appreciable in-plane covalency in the molecule. The calculated value of $(g_{\parallel}/A_{\parallel})$ for the complexes is characteristic of distorted structure. The poor in-plane π bonding in the complexes is reflected in their β^2 values. The molecular orbital coefficients α^2 and β^2 were calculated using

the Kivelson and Neiman formula [39] (Supplementary Figures 9 and 10):

$$\alpha_{Cu}^2 = \frac{A_{\parallel}}{p} + (g_{\parallel} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04, \quad (1)$$

$$\beta_{Cu}^2 = \frac{(g_{\parallel} - 2.0023)E}{(-8\lambda\alpha^2)}.$$

3.6. Fluorescence Study. The fluorescent nature of 3-(aryl)-pentane-2,4-dione (**L1** and **L2**) and its metal(II) complexes are shown in Table 6. Ligands have been inferred from their emission bands around 379, 498 nm. The metal(II) complexes of all the above ligands also exhibit three emission bands in the range of 486–796 nm. Significant differences in the positions of emissions maximum of 3-(aryl)-pentane-2,4-dione and its complexes establish the complexation process [40]. 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 and electronic energy transfer [41]. 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 onto the metal orbital via complex formation which causes a suppression of this fluorescence intensity [42] (Supplementary Figures 11 and 12).

3.7. NLO Property of 3-(Aryl)-pentane-2,4-dione. The SHG (second harmonic generation) efficiency of the two different acetylacetone-based Knoevenagel condensates is presented in Table 7. The SHG efficiency of the ligands **L1** and **L2** is better than that of the references (KDP and urea). The output energy for SHG is 4 mV, 3 mV, 13 mV, and 57 mV, respectively, for **L1**, **L2**, KDP, and urea. In general a molecule with delocalized π -electron system can have large nonlinear polarizabilities [43] and it has generally understood that the molecular nonlinearity can be enhanced by systems with strong donor and acceptor groups [44]. From the analysis of electronic transitions and molecular orbital involved, ligand orbital can improve the NLO properties.

TABLE 7: SHG parameters of different Knoevenagel condensates of 3-(aryl)-pentane-2,4-dione.

Compound	SHG efficiency with respect to KDP	SHG efficiency with respect to urea
L1	0.3	0.07
L2	0.2	0.05

TABLE 8: Antimicrobial activity of the ligands **L1** and **L2** and their metal(II) complexes (zone of inhibition in mm^{**}; concentration in 10⁻³ mol/L).

Compound	<i>P. aeruginosa</i>		<i>S. aureus</i>		<i>E. coli</i>		<i>C. albicans</i>	
	L1	L2	L1	L2	L1	L2	L1	L2
Ligand (L)	8	10	8	6	8	5	8	8
a -Cu(II) complex	14	16	15	10	9	9	11	11
b -Co(II) complex	11	17	14	16	9	9	11	11
c -Ni(II) complex	8	17	12	14	R	9	10	10
Standard	18		18		18		12	

** Its value observed is within the error limits of ± 1 . R: resistance.

3.8. *Biological Activity.* Zone-of-inhibition values of the investigated compounds against the *bacteria and fungus* are summarized in Table 8. Amikacin and ketoconazole have been used as reference compounds for antibacterial and antifungal activities, respectively. The observed values indicate that most of the complexes have higher activity than the free ligand. Such an increased activity of the complexes can be explained on the basis of chelation theory [45]. 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 [46–48] 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.

4. Conclusion

A novel type of Knoevenagel condensate has been synthesized from acetylacetone, and various substituted aromatic aldehydes and their metal complexes for M:L ratio 1:1 of Cu(II), Co(II), and Ni(II) were obtained. An octahedral structure has been proposed for all the metal(II) complexes except copper(II) (**L2a**), cobalt(II) (**L2b**), and nickel(II) (**L2c**) which showed square planar structure. Though some Knoevenagel condensed complexes have been found in the recent literature [47], these have been rarely seen as nonlinear optical materials in terms of second harmonic generation (SHG) efficiency. In our system the ligands **L1** and **L2** of Knoevenagel condensate are found to exhibit considerable

nonlinear optical (NLO) property in comparison with urea and KDP. All the ligands and their metal(II) complexes are fluorescent in nature. Metal(II) complexes exhibited a considerable antimicrobial activity compared to the free ligands.

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