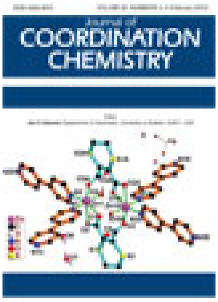
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:43
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, spectral, NLO studies, and antimicrobial activities of curcumin diketimine metal complexes

S. Sumathi [a], P. Tharmaraj [a], C.D. Sheela [b] & R. Ebenezer [a]

[a] Department of Chemistry, Thiagarajar College, Madurai - 625 009, India

[b] Department of Chemistry, The American College, Madurai - 625 002, India

Published online: 30 Jan 2012.

To cite this article: S. Sumathi, P. Tharmaraj, C.D. Sheela & R. Ebenezer (2012) Synthesis, spectral, NLO studies, and antimicrobial activities of curcumin diketimine metal complexes, Journal of Coordination Chemistry, 65:3, 506-515, DOI: 10.1080/00958972.2012.655727

To link to this article: http://dx.doi.org/10.1080/00958972.2012.655727

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Journal of Coordination Chemistry
Vol. 65, No. 3, 10 February 2012, 506–515

Synthesis, spectral, NLO studies, and antimicrobial activities of curcumin diketimine metal complexes

S. SUMATHI†, P. THARMARAJ*†, C.D. SHEELA‡ and R. EBENEZER†

†Department of Chemistry, Thiagarajar College, Madurai – 625 009, India
‡Department of Chemistry, The American College, Madurai – 625 002, India

(*Received 7 September 2011; in final form 9 December 2011*)

A series of metal(II) complexes ML [where M = Cu(II), Co(II), Ni(II), Zn(II)] have been prepared from [4-((1H-indol-3-yl)methylene)-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione] (IMHH) and 2,4-diamino-6-phenyl-1,3,5-triazine. The structures of the complexes have been investigated by using elemental analysis, magnetic susceptibility, molar conductance, IR, UV-Vis, mass, NMR, and ESR spectral studies. Conductivity measurements reveal that all the complexes are electrolytes. Spectral and other data show either octahedral or square-pyramidal geometry for all the complexes. Redox behavior of the copper(II) complex has been studied through cyclic voltammetry. Antimicrobial activities of the compounds were studied against several microorganisms with all the complexes having higher activity than free ligand. All the compounds may serve as potential photoactive materials as indicated from their fluorescence properties. The second harmonic conversion efficiency of the ligand has been found to be higher than that of urea and KDP.

Keywords: Curcumin; Indole-3-aldehyde; s-Triazine; Metal(II) complexes; Fluorescence; SHG

1. Introduction

Curcumin, also known as diferuloylmethane, is a natural carotenoid pigment used as a traditional medicine for treatment of gastrointestinal disorders, hepatic disorders, diabetic wounds, skin wounds, and rheumatism [1]. Curcumin and its analogs show remarkable pharmacological activities, including anti-inflammatory, anticarcinogenic, antioxidant activity, and anti-HIV-1 [2–6]. Curcumin exhibits protective effects against oxidative damage and is a potent cancer chemo preventive agent [7]. Recently, it has been considered as a key molecule for development of novel therapeutics for Alzheimer's disease [8].

Curcumin is also a food coloring and flavoring agent approved by the Food and Drug Administration. It has a diketone moiety with a highly conjugated side chain. Generally molecules with conjugated π-electron systems can have large nonlinear polarizabilities [9] and nonlinear optical (NLO) materials have important roles in a wide range of photonic applications [10, 11]. In an attempt to promote the NLO response of curcumin, 2,4-diamino-6-phenyl-1,3,5-triazine was introduced into a Schiff base.

---

*Corresponding author. Email: ptharma@rediffmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.655727

Since curcumin is well-known for its medicinal value and conjugated side chain, condensation of the active methylene of the β-diketone with an aldehydic group will give a non-enolisable Knoevenagel condensate, which can effectively react with amines to form Schiff bases [12]. Our aim is to synthesize compounds with nonlinear properties and pharmacological activities. In this work, we present the characterization, biological screening, NLO properties, and fluorescence of curcumin diketimines and metal complexes derived from 4-((1H-indol-3-yl)methylene)-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione (IMHH) and 2,4-diamino-6-phenyl-1,3,5-triazine.

2. Experimental

All chemicals and solvents were purchased from commercial sources. Curcumin and indole-3-aldehyde were obtained from E. Merck. 2,4-Diamino-6-phenyl-1,3,5-triazine was obtained from Aldrich and used as supplied. Solvents were double distilled and stored in molecular sieves (4Å) before use. For voltammetric experiments, tetrabutylammonium perchlorate (TBAP) (Sigma) was used as supporting electrolyte. Nuclear magnetic resonance (NMR) measurement was made on a BRUKER 300 MHz spectrometer. UV-Vis spectra were recorded on a THERMO SPECTRONIC 6 HEXIOS α and fluorescence spectra were performed on an ELICO SL174 spectrofluorometer using DMSO. Electron impact (EI) mass spectra were recorded by a GEOL-GC MATE-2 mass spectrometer. Infrared (IR) spectra were carried out by using a SHIMADZU FTIR 8400 spectrophotometer. Electron spin resonance (ESR) spectra of the copper(II) complex 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 study for the Cu(II) complex was taken on a CH Instrument (USA). Molar conductances of the complexes were measured in DMSO at room temperature using a Systronic Conductivity Bridge 304. All complexes were screened for biological activity with the well diffusion method. The second harmonic generation (SHG) conversion efficiency of 4-((1H-indol-3-yl)methylene)-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione (IMHH) and the curcumin diketimine Schiff base were determined by a modified version of powder technique (IISc, Bangalore).

2.1. *Synthesis of Knoevenagel condensate (IMHH)*

The non-enolisable diketone was prepared by employing the modified procedure reported earlier [13]. Curcumin (3.7 g, 1 mmol) was mixed with indole-3-aldehyde (1.4 g, 1 mmol) and piperidine ($0.05\,\mathrm{cm}^3$) in ethanol (50 mL), and the reaction mixture was stirred thoroughly for 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 recrystallized from ethanol to give a yellow solid Knoevenagel condensate. Yield: 78%, m.p: 105°C [^{1}H NMR, 3.92 δ (s, 6H, –OCH_3), 6.50–7.85 δ (m, aromatic proton), 8.31 δ (s, 1H, –C=CH–), 9.06 δ (s, 1H, –NH–)]. The EI mass spectrum of the

Knoevenagel condensate (IMHH) gives a molecular ion peak *m*/*z* at 495 (Supplementary material).

2.2. *Synthesis of curcumin diketimine Schiff base*

A mixture of IMHH (2.5 g, 1 mmol) and 2,4-diamino-6-phenyl-1,3,5-triazine (1.9 g, 2 mmol) in ethanol solution was stirred for 6 h at room temperature and in the presence of piperidine for a period of 6 h [12]. The solution was concentrated with a rotovaporator and the resulting residue was refrigerated overnight. The reddish yellow solid was filtered and recrystallized from ethanol. Yield: 72%, m.p: 172°C [^{1}H NMR, 3.95 δ (s, 6H, $-OCH_3$), 6.50–7.85 δ (m, aromatic proton), 8.33 δ (s, 1H, $-C{=}CH-$), 9.08 δ (s, 1H, $-NH-$), 3.95 δ (s, 2H, $-NH_2$)]. The EI mass spectrum of the curcumin diketimine Schiff base gave a molecular ion peak *m*/*z* at 833 (Supplementary material).

2.3. *Synthesis of metal(II) complexes*

The metal complexes were prepared by addition of hot solution of the appropriate metal chloride (1 mmol) in ethanol (25 mL) to hot solution of the curcumin diketimines (0.5 g, 1 mmol) in the same solvent (25 mL). The resulting mixture was stirred under reflux for 1 hour whereupon the complex precipitated was collected by filtration, washed thoroughly with ethanol, and dried in vacuum.

2.4. *NLO properties of ligand*

SHG efficiency, also called frequency doubling, is an NLO process in which photons interacting with a nonlinear material are effectively combined to form new photons with twice the energy and therefore twice the frequency and half the wavelength of the initial photons. It is a special case of sum frequency generation. For powder samples Kurtz and Perry modified the SHG efficiency determination method [14]; this modified method was employed for IMHH and curcumin diketimine Schiff base to determine its SHG value which in turn was compared with microcrystalline powders of KDP and urea. The finely ground sample was packed between transparent glass slides and a laser beam of wavelength 1064 nm from Nd : YAG source was directed on the sample cell. The incident and residual light of 1064 nm was filtered by copper sulfate solution and Filter BG-38, respectively. The 532 nm central wavelength had an interference filter band with a width of 4 nm. The photomultiplier detects green light emitted by the NLO active sample and the quantified value gets displayed on the storage oscilloscope. An input energy of 2.2 mJ pulse^{-1} was used in this particular setup.

2.5. *Biological activity*

Antimicrobial activities of the compounds were tested *in vitro* by the well diffusion method [15] against *Streptococcus pyogenes* and *Staphylococcus aureus* using agar nutrient as the medium; antifungal activities against *Aspergillus flavus* and *Penicillium digitatum* cultured on potato dextrose agar as medium were tested. About 0.5 mL spore

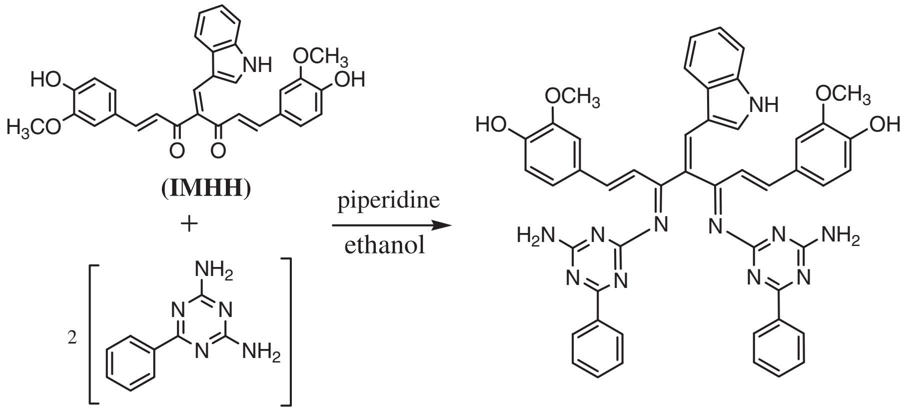


Figure 1. Synthesis of the Schiff base.

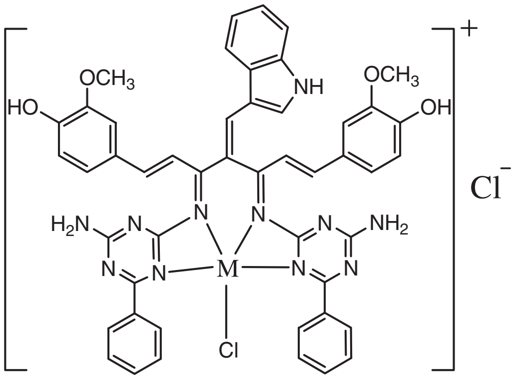
Table 1. Analysis, molar conductance, and magnetic susceptibility data of the Schiff base and metal(II) complexes.

		Calculated (Found) %					
Compound	m.p. (°C)	M	C	H	N	Conductance ($S\,cm^2\,m^{-1}$)	μ_{eff} (B.M.)
Schiff base	172–173	–	69.1(69.0)	4.7(4.5)	18.5(18.4)	–	–
[CuLCl]Cl	193–195	6.5(6.3)	59.7(59.5)	4.1(4.0)	15.9(15.8)	56	1.99
[CoLCl]Cl	206–208	6.1(6.0)	59.9(59.6)	4.0(3.9)	16.0(15.8)	63	4.90
[NiLCl]Cl	215–217	6.2(6.0)	59.8(59.7)	4.1(3.9)	15.9(15.7)	59	3.02
[ZnLCl]Cl	220–222	6.7(6.4)	59.4(59.2)	4.2(4.0)	15.8(15.7)	60	–

suspension of each organism was added to sterile petri dishes and left to solidify; the well was made in each plate with the help of a cork-borer (6 mm). The stock solution ($10^{-3}\,mol\,L^{-1}$) was prepared by dissolving the compounds in DMSO. The plates were inoculated with microorganisms and filled with the test solution (24 h for bacteria and 48 h for fungus) at 37°C. The activities were measured as zones of inhibition against bacteria and fungi appearing around the well.

3. Results and discussion

The analytical data and physical properties of the curcumin diketimine Schiff base (figure 1) and metal complexes are presented in table 1. The molar conductances of the complexes imply that all the complexes are electrolytes. The metal(II) complexes are air stable, non-hydroscopic, intensely colored, and amorphous solids. They are freely dissolved in acetonitrile, DMSO, and DMF. The analytical data of the complexes are in good agreement with the general formula [MLCl]Cl, where M = Cu(II), Ni(II), Co(II), Zn(II). The obtained magnetic moment data show the paramagnetic behavior of Cu(II), Co(II), and Ni(II). The magnetic moments of the complexes are consistent with either octahedral or square-pyramidal geometry around central metal ion (figure 2).



M = Cu(II), Co(II), Ni(II), Zn(II)

Figure 2. Proposed structure of metal(II) complexes.

Table 2. IR spectral data (in cm^{-1}) of the Schiff base and metal(II) complexes.

Compound	ν(C=N)	ν(C–N)	ν(M–N)
Schiff base	1649	830	–
[CuLCl]Cl	1635	818	429
[CoLCl]Cl	1631	825	428
[NiLCl]Cl	1633	821	454
[ZnLCl]Cl	1630	823	464

3.1. *Mass spectra*

In the mass spectra of curcumin diketimine Schiff base and metal(II) complexes, the molecular ion peak for the ligand was observed at 833 m/z whereas the M+ peak for copper(II) and cobalt(II) were obtained at 967 and 963 m/z, respectively, corresponding to [MLCl]Cl. The peaks at m/z 932 and 928 are $[MLCl]^+$ formed by loss of a chlorine radical from the molecular ion of respective metal complexes (Supplementary material).

3.2. *IR spectra*

IR spectral data of the ligand and complexes are listed in table 2. The band at 1649 cm^{-1} is characteristic of the azomethine group. In complexes this strong band shifts to 1630–1635 cm^{-1} corresponding to ν(C=N) due to coordinated azomethine [13]. The ligand shows a strong band at 830 cm^{-1} characteristic of ν(C–N) group in s-triazine. The band shift to 825–818 cm^{-1} upon complexation indicates that the group [16] is coordinated. The IR spectrum of the Schiff base exhibits a band at 3185 cm^{-1} assignable to ν(NH_2). The appearance of this mode at almost the same frequency in all the complexes suggests that the above group does not coordinate. Bands at 3441 and 2935 cm^{-1} are attributed to ν(–OH) and ν(–NH), respectively, almost unchanged in the complexes, indicating that this group is not participating in coordination [17]. In the metal complexes, there is a new band at 428–464 cm^{-1} assigned to ν(M–N) [18]. Bands observed at 310–325 cm^{-1} in the complexes were attributed to ν(M–Cl) [19].

Table 3. Electronic spectral data of metal(II) complexes.

Compound	Frequency (ε) (cm^{-1})	Transition	Geometry
[CuLCl]Cl	11,006 (956)	$^2B_1 \rightarrow {}^2A_1$	Square-pyramidal
	14,920 (1005)	$^2B_1 \rightarrow {}^2B_2$	
	17,006 (1158)	$^2B_1 \rightarrow {}^2E$	
[CoLCl]Cl	10,881 (548)	$^4A_2 + {}^4E \rightarrow {}^4B_1$	Square-pyramidal
	17,847 (856)	$^4A_2 + {}^4E \rightarrow {}^4E(P)$	
	20,008 (1426)	$^4A_2 + {}^4E \rightarrow {}^4A_2(P)$	
[NiLCl]Cl	10,373 (471)	$^3B_1(F) \rightarrow {}^3E(F)$	Square-pyramidal
	18,227 (852)	$^3B_1(F) \rightarrow {}^3A_2(P)$	
	23,364 (1653)	$^3B_1(F) \rightarrow {}^3E(P)$	

3.3. *Electronic spectra*

Electronic absorption spectral data of the complexes recorded in DMSO are given in table 3. The UV-Vis spectrum of the copper(II) complex shows bands at 11,006, 14,920, and 17,006 cm^{-1}, assigned to the transitions $^2B_1 \rightarrow {}^2A_1(\nu_1)$, $^2B_1 \rightarrow {}^2B_2(\nu_2)$, and $^2B_1 \rightarrow {}^2E(\nu_3)$, respectively, characteristic of square-pyramidal geometry [20–22]. The copper(II) complex at 1.99 B.M. is suggestive of a five-coordinate square-pyramidal geometry. The magnetic moment value and spectral data confirm square-pyramidal geometry around copper [23].

Electronic absorption spectrum of the Co(II) complex displayed bands at 10,881, 17,847, and 20,008 cm^{-1} which can be assigned to the transitions $^4A_2 + {}^4E \rightarrow {}^4B_1$, $^4A_2 + {}^4E \rightarrow {}^4E(P)$, and $^4A_2 + {}^4E \rightarrow {}^4A_2(P)$, respectively, characteristic of square-pyramidal geometry [24]. The nickel(II) complex exhibits three d–d bands at 10,373, 18,227, and 23,364 cm^{-1}, assigned as $^3B_1(F) \rightarrow {}^3E(F)$, $^3B_1(F) \rightarrow {}^3A_2(P)$, and $^3B_1(F) \rightarrow {}^3E(P)$ transitions, respectively, suggesting square-pyramidal geometry. The spectra resemble those reported for five-coordinate, square-pyramidal nickel(II) complexes [25, 26]. Co(II) and Ni(II) complexes have magnetic moment values of 4.90 and 3.02 B.M, respectively, further confirming the square-pyramidal geometry [27, 28].

3.4. *Electrochemical behavior*

The cyclic voltammograms of the copper(II) complex are recorded at room temperature using TBAP as the supporting electrolyte from 0.8 to −0.5 V. The peak current for the complex varies with scan rates and the $E_{pa} - E_{pc}$ values are greater than 200 mV, which indicates that the reduction processes are irreversible [29] and the ratio of anodic to cathodic peak currents corresponding to the chemical change occurs with the electron transfer as Cu(II) → Cu(III) → Cu(II) → Cu(I) at $E_{pa} = 0.345$ V and $E_{pc} = 0.094$ V.

3.5. *EPR spectra*

The EPR spectrum of the copper(II) complex recorded in DMSO at 300 and 77 K and the spin Hamiltonian parameters of the complex are listed in table 4. The observed spectral parameters show $g_{\parallel} > g_{\perp}$ characteristic of an axially elongated square-pyramidal geometry [30]. The covalent character of metal–ligand bond is inferred from the g_{iso} value 2.14, which supports the unpaired electron lying predominantly in the

Table 4. The spin Hamiltonian parameters of copper(II) complex.

Complex	A_{iso} (10^{-4}cm^{-1})	g_{iso}	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (10^{-4}cm^{-1})	$A_{\perp}$ (10^{-4}cm^{-1})	α^2	β^2	$g_{\parallel}/A_{\parallel}$ (cm)
[CuLCl]Cl	145	2.14	2.32	2.13	171.4	37.2	0.45	2.41	133.6

Table 5. Fluorescence parameters of the Schiff base and its metal(II) complexes in DMSO.

Compound	Emission maximum (nm)
Schiff base	483, 548
[CuLCl]Cl	550, 582, 596
[CoLCl]Cl	551, 589, 592
[NiLCl]Cl	554, 585, 598
[ZnLCl]Cl	550, 586, 594

$d_{x^2-y^2}$ orbital. G is estimated from the expression $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ as 2.11, suggesting an exchange coupling is present and misalignment appreciable. The calculated magnetic moment for the copper(II) complex using the relation $\mu^2 = 3/4\ |g|^2$ is indicative of an unpaired electron. The α^2 value (0.45) indicates appreciable in-plane covalency in the molecule. The calculated value of ($g_{\parallel}/A_{\parallel}$) 133.6 cm for the complex is characteristic of a distorted structure [31]. 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:

$$\alpha^2_{Cu} = A_{\parallel}/p + \left(g_{\parallel} - 2.0023\right) + 3/7(g_{\perp} - 2.0023) + 0.04$$
$$\beta^2_{Cu} = \left(g_{\parallel} - 2.0023\right)E/\left(-8\lambda\alpha^2\right).$$

3.6. *Fluorescence study*

The fluorescent nature of curcumin diketimine Schiff base and its metal(II) complexes are shown in table 5. Ligand has emission bands at 483 and 548 nm. The metal(II) complexes exhibit three emission bands at 550–598 nm. Significant differences in positions of emission maxima of ligand and its complexes establish complex formation [32]. All the complexes have broad emission bands indicating charge transfer. Quenching of fluorescence of ligand by transition metal ions during complexation is common from redox activity and electronic energy transfer [33]. Enhancement of fluorescence through complexation opens the opportunity for photochemical applications of these complexes [34].

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

The SHG efficiency of IMHH and curcumin diketimine Schiff base shows much higher efficiency than KDP and urea. This may be due to the presence of indole and triazine;

Table 6. Antimicrobial activity of the Schiff base and its metal(II) complexes (zone of inhibition in mm**; concentration in 10^{-3} mol L^{-1}).

Compound	*S. pyogenes*	*S. aureus*	*A. flavus*	*P. digitatum*
Schiff base	11	10	8	11
[CuLCl]Cl	12	23	10	17
[CoLCl]Cl	16	14	10	13
[NiLCl]Cl	15	13	12	13
[ZnLCl]Cl	15	12	11	14
Standard	20	18	18	19

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

molecules with delocalized π-electron systems can have large nonlinear polarizabilities [35] and molecular nonlinearity can be enhanced by systems with strong donor and acceptor groups [36]. The second harmonic efficiency measurements clearly reveal that IMHH possesses 0.3 times better activity than that of urea and 1.2 times more activity than KDP. Similarly, curcumin diketimine Schiff base shows 0.5 and 2.2 times more activity than urea and KDP, respectively. Metal(II) complexes are much lower than the references (KDP and urea).

3.8. *Biological activity*

Zone of inhibition values against the bacteria and fungi are summarized in table 6. Amikacin and Fluocinolone have been used as reference compounds for antibacterial and antifungal activities, respectively. The observed values indicate that most of the complexes possess higher activity than the free ligand. The antibacterial activity of Cu(II) complex is more than amikacin against *S. aureus*. Hence, copper(II) complex is more effective against microbes. Similar studies [37] reveal that Cu(II) complex is relatively potent against proliferation in human leukemic cells. Increased activity of the complexes can be explained on the basis of chelation theory [38, 39] and size of the metal ion. On chelating, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the ligand orbital and donor groups. The mode of the action of compounds may involve formation of hydrogen bond with the active center of cell constituents resulting in interference with normal cell processes.

4. Conclusion

Curcumin diketimine Schiff base complexes [ML] of Cu(II), Co(II), Ni(II), and Zn(II) derived from 4-((1H-indol-3-yl)methylene)-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione (IMHH) and 2,4-diamino-6-phenyl-1,3,5-triazine were synthesized and characterized by spectral and analytical data. IMHH and curcumin diketimine Schiff base exhibit appreciable nonlinear property and can be utilized for further NLO investigations; the metal(II) complexes exhibit very low second harmonic efficiency (SHG) in comparison with KDP and urea. Although some NLO active triazine compounds have been found in the literature [40], these compounds have been rarely used as NLO materials for SHG efficiency. Most of the metal chelates show better antimicrobial activity than curcumin diketimine Schiff base; particularly Cu(II) has higher antibacterial activity against *S. aureus* than the standard. Such increased activity of the metal complex is of importance in pharmaceutics. Schiff base and its metal(II) complexes are fluorescent.

Acknowledgments

The authors thank the Management of Thiagarajar College, Madurai and one of the authors (PT) thanks the Defence Research and Development Organization (DRDO), New Delhi for providing financial support and SAIF, IIT, Bombay and SAIF, CDRI, Lucknow for analytical facilities.

References

[1] J. Hong, M. Bose, J. Ju, J.-H. Ryu, X. Chen, S. Sang, M.-J. Lee, C.S. Yang. *Carcinogenesis*, **25**, 1671 (2004).
[2] V. Eybl, D. Kotyzova, M. Bludovska. *Toxicol. Lett.*, **151**, 79 (2004).
[3] J.K. Lin, S.Y. Lin-Shiau. *Proc. Natl. Sci. Commun.*, **25**, 59 (2001).
[4] A.L. Cheng, C.H. Hsu, J.K. Lin, M.M. Hsu, Y.F. Ho, T.S. Shen, J.Y. Ko, J.T. Lin, B.R. Lin, W. Ming-Shiang, H.S. Yu, S.H. Jee, G.C. Chen, T.M. Chen, C.A. Chen, M.K. Lai, Y.S. Pu, M.H. Pan, Y.J. Wang, C.C. Tsai, C.Y. Hsieh. *Anticancer Res.*, **21**, 2895 (2001).
[5] L. Barclay, R. Vinqvist, K. Mukai, H. Goto, Y. Hasimoto, A. Tokunaga, H. Uno. *Org. Lett.*, **2**, 2841 (2000).
[6] A. Mazumder, N. Neamati, S. Sunder, J. Schulz, H. Pertz, E. Eich, Y. Pommier. *J. Med. Chem.*, **40**, 3057 (1997).
[7] B. Aggarwal, A. Kumar, M. Aggarwal, S. Shishodia. In *Phytopharmaceuticals in Cancer Chemoprevention*, P. D. Debasis Bagchi, H.G. Preuss (Eds.), p. 349, CRS Press, New York (2005).
[8] D. Yanagisawa, N. Shirai, T. Amatsubo, H. Taguchi, K. Hirao, M. Urushitani, S. Morikawa, T. Inubushi, M. Kato, F. Kato, K. Morino, H. Kimura, I. Nakano, C. Yoshida, T. Okada, M. Sano, Y. Wada, K-N. Wada, A. Yamamoto, I. Tooyama. *Biomaterials*, **31**, 4179 (2010).
[9] M. Jalali Heravi, A.A. Khandar, I. Sheikshoaie. *Spectrochim. Acta, Part A*, **55**, 2537 (1999).
[10] K. Rurack, J.L. Bricks, G. Reck, R. Radeglia, U. Resch Genger. *J. Phys. Chem.*, **104**, 3087 (2000).
[11] Z. Xu, G. Bai, C. Dong. *Bioorg. Med. Chem.*, **13**, 5694 (2005).
[12] P. Annaraj, M. Ponvel, P. Athappan. *Transition Met. Chem.*, **29**, 722 (2004).
[13] S. Srinivasan, G. Rajagopal, P.R. Athappan. *Transition Met. Chem.*, **26**, 588 (2001).
[14] S.K. Kurtz, T.T. Perry. *J. Appl. Phys.*, **39**, 3798 (1968).
[15] O.N. Irobi, M. Moo-Young, W.A. Anderson. *Int. J. Pharm.*, **34**, 87 (1996).
[16] A. Solankee, I. Thakor. *Indian J. Chem.*, **45B**, 517 (2006).
[17] B.B. Subudhi, P.K. Panda, S. Sahoo. *Iran. J. Pharm. Sci. Autumn*, **3**, 245 (2007).
[18] R.M. Issa, S.A. Azim, A.M. Khedr, D.F. Draz. *J. Coord. Chem.*, **62**, 1859 (2009).
[19] Y. Jadegoud, O.B. Ijare, B.S. Somashekar, G.A. Nagana Gowda, B.H.M. Mruthyunjayaswamy. *J. Coord. Chem.*, **61**, 508 (2008).
[20] A. Koji, K. Matsfuji, M. Ohba, H. Okawa. *Inorg. Chem.*, **41**, 4461 (2002).
[21] M. Handa, T. Idehara, K. Nakano, K. Kasuga, M. Mikuriya, N. Matsmoto, M. Kodera, S. Kida. *Bull. Chem. Soc. Japan*, **65**, 3241 (1992).
[22] Y. Yamada, H. Sakurai, Y. Miyashita, K. Fujisawa, K.I. Okamoto. *Polyhedron*, **21**, 2143 (2002).
[23] E.R. Acuria Cueva, R. Faure, A. Nuria, I. Cabeza, B. Sonia, J. Pulido, N. Miguel, M. Carretero, M. Quiros Olozabal. *Inorg. Chim. Acta*, **351**, 356 (2003).
[24] L.K. Gupta, S. Chandra. *Spectrochim. Acta, Part A*, **65**, 792 (2006).
[25] S.M.E. Khalil. *J. Coord. Chem.*, **56**, 1013 (2003).
[26] P. Yang, Y. Yang, C. Zhang, X.J. Yang, H.M. Hub, Y. Gao, B. Wu. *Inorg. Chim. Acta*, **362**, 89 (2009).

[27] S. Chandra, D. Shukla. *J. Saudi Chem. Soc.*, **9**, 545 (2005).
[28] Otta Dahl. *Acta Chem. Scand.*, **23**, 2342 (1962).
[29] R. Kannappan, R. Mahalakshmy, T.M. Rajendran, R. Venkatesan, P. Sambasiva Rao. *Proc. Indian Acad., (Chem. Sci)*, **115**, 1 (2003).
[30] R.K. Ray, G.B. Kauffman. *Inorg. Chim. Acta*, **153**, 207 (1990).
[31] V.T. Kasumov, F. Koksal. *Spectrochim. Acta, Part A*, **60**, 31 (2004).
[32] A. Majumder, M. Georgina, R. Arabinda Mallick, N. Chattopadhyay, S. Mitra. *Polyhedron*, **25**, 1753 (2006).
[33] N. Chattopadhyay, A. Mallick, S. Sengupta. *J. Photochem. Photobiol.*, **177**, 55 (2005).
[34] P. Purkayastha, G.K. Patra, D. Datta, N. Chattopadhyay. *Indian J. Chem.*, **39**, 375 (2000).
[35] M. Jalali Heravi, A.A. Khandar, I. Sheikshoaie. *Spectrochim. Acta, Part A*, **55**, 2537 (1999).
[36] P.S. Patil, S.M. Dharmaprakash, K. Ramakrishna, H.-K. Fun, R. Sai Santosh Kumar, D. Narayana Rao. *J. Cryst. Growth*, **303**, 520 (2007).
[37] A.P. Zambre, V.M. Kulkarni, S. Padhye, S.K. Sandur, B.B. Aggarwal. *Bioorg. Med. Chem.*, **14**, 7196 (2006).
[38] C.D. Sheela, C. Anitha, P. Tharmaraj, D. Kodimunthri. *J. Coord. Chem.*, **63**, 884 (2010).
[39] M. Muthukumar, P. Viswanathamurthi. *J. Coord. Chem.*, **63**, 1263 (2010).
[40] Y.Z. Cui, Q. Fang, H. Lei, G. Xue, W.T. Yu. *Chin. Chem. Lett.*, **14**, 856 (2003).