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Synthesis and Spectroscopic Characterization of Some New Coordination Compounds of Organotin (IV) with Carbohydrazones

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Abstract

Some new coordination compounds of tin(IV) having general formula $[SnBu_2(L)_2]$ (where L = carbohydrazone ligand) have been synthesized by the reaction of dibutyltin oxide with carbohydrazone ligands with the ratio of 1:2 (metal- ligand) using dry benzene as a reaction medium. The newly synthesized complexes were characterized by elemental analysis, molecular weight determinations, conductivity measurement and spectral analysis *viz*., IR, UV-Vis and NMR (^1H, ^{13}C and ^{119}Sn). A distorted octahedral geometry of these complexes has been assigned on the basis of spectral studies. The biological activities of carbohydrazones and their Sn(IV) complexes have been screened in vitro against some bacterial and fungal strain to assess their growth inhibitory potency. Most of the metal complexes exhibit more antibacterial and antifungal activities than the free carbohydrazone ligands against these organisms.

Keywords: *Dibutyltin oxide, carbohydrazones, spectral analysis, biological activities.*

Introduction

Carbohydrazones are known to be a class of versatile ligands in coordination chemistry due to their ease of synthesis and diversity as well as structural possibilities. According to literature, they have been also as potent antimicrobial, antioxidant, therapeutic, anticonvulsant, cytotoxic and pharmacological as well as catalytic agents [1-4]. Carbohdrazone ligands synthesize by using carbohydrazide having enormous biological applications due to their oxygen and nitrogen donor atoms. Carbohydrazones exist in equilibrium of various tautomers due to unique structural

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features which greatly affect their chelating ability [5].

Organometallic complexes of tin(IV) play a special role, due to their structural diversity. The chemistry of organotin(IV) derivatives is important due to their wide range of applications. The increasing importance of organotin(IV) complexes is due to their wide spread use in plastic industries such as PVC stabilizing agents [6] and antineoplastic agents [7] also broadly use in coating of ship hulls [8] and marine antifouling agents [9]. Organotin complexes are commonly used in agricultural field as wood preservatives10, fungicides [11] and insecticides [12]. Organotin complexes exhibit pharmacological applications such as bacteriocides [13] as an antitumor [14-19] agents as an antimicrobial agents [20-22] as an anti-inflammatory agents [23] as an antiviral agents [24-25] as an anti-tuberculosis agents [26] and as an antihelmintics [27] and so on. Some of organotin(IV) derivatives containing O-O' bidentate donors showed strong antitumor activity than of cis-platin and mitomycin-C [28].

Continuing earlier research [29] on biologically active complexes, systematic studies on the binding of carbohydrazones to Sn(IV) metal ion lead to the conception to develop new and efficient complexes, play a vital role in a vast number of biological process. In view of these facts, here we were thus motivated to undertake a systematic study of preparation and structural characterization of some new Sn(IV) complexes formed with carbohydrazones (LH) and Sn(IV) ion. In addition, the biological studies were applied to the free ligands and their Sn(IV) complexes against different bacterial, fungal strains using inhibitory zone diameter.

Experimental

Materials

Solvents were dried by standard methods [30] before use. Bu2SnO (Aldrich) has been used as supplied. The ligands used in this study have been synthesized in the laboratory using standard method reported in the literature [31].

Physical measurements

Melting points were recorded on Gallenkamp melting point apparatus. IR spectra have been recorded using 8400 Shimadzu FT-IR Spectrophotometer using KBr pellets in the range of 4000-400 cm^{-1}. ^{1}H and ^{13}C NMR in $CDCl_3$ solution were recorded with a JEOL-FT A1 300 MHz spectrometer using TMS an internal reference. ^{119}Sn NMR spectra with proton noise decoupling in dry DMSO as the solvent, were recorded on a 90 MHz JEOL spectrometer using TMT (tetramethyltin) an internal reference. Micro analytic data for (C, H, N) were recorded on a Coleman 5612 analyzer. The UV-Vis spectra of the carbohydrazones and their Sn(IV) complexes were recorded on a 1800 Shimadzu UV

spectrophotometer in the range of 200-800 nm. Molecular weights were determined by Rast method. All the compounds have been synthesized using similar method therefore the synthetic and analytical data of the prepared complexes have been summarized in Table 1.

Table 1. Physical data of Sn(IV) complexes of carbohydrazones.

Cmpd.	Yield (%)	M.P. (^oC)	Color	Elemental analysis (%)				M:L in dry benzene	Mol. Wt. Found (Calcd.)
				C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	Sn Found (Calcd.)		
$Sn[(C_{40}H_{58}N_{10}O_4)]$	65	130	Brown	55.79 (55.76)	6.79 (6.78)	16.27 (16.26)	13.79 (13.78)	1:2	861.15 (861.66)
$Sn[(C_{46}H_{58}N_{10}O_4)]$	70	145	Gray	59.18 (59.17)	6.26 (6.26)	15.00 (15.00)	12.71 (12.71)	1:2	933.65 (933.73)
$Sn[(C_{36}H_{50}N_{10}O_4)]$	65	150	Dark green	53.69 (53.68)	6.26 (6.27)	17.39 (17.39)	14.74 (14.74)	1:2	805.35 (805.55)
$Sn[(C_{44}H_{54}N_{10}O_4)]$	80	140	Dark brown	58.36 (58.35)	6.01 (6.00)	15.47 (15.47)	13.11 (13.11)	1:2	905.50 (905.67)
$Sn[(C_{38}H_{54}N_{10}O_4)]$	72	135	Green	54.77 (54.75)	6.53 (6.53)	16.81 (16.80)	14.25 (14.24)	1:2	833.30 (833.61)

Synthesis of carbohydrazones

Carbohydrazones have been synthesized by refluxing the reaction mixture of hot ethanolic solution of carbohydrazide and hot ethanolic solution of suitable carbonyls viz., salisylaldehyde,2-hydroxy-1-nephthaldehyde, *o*-hydroxyacteophenone, 2-hydroxy-1-acteonaphthone, o-hydroxypropiophenone and 2-acetylpyrrole in 1:1:1 molar ratio for 2 h. The products obtained after the evaporation of the solvent were filtered and recrystallized from ethanol.

Synthesis of complexes (A^1-A^5) of carbohydrazones

The reactions of dibutyltin oxide with ligand have been carried out in 1:2 molar ratios in dry benzene. The reaction mixture was heated under reflux on a fractioning column for 8-10 h. After the completion of reaction, the excess solvent was removed under reduced pressure to yield coloured viscous liquid (yield 65-80 %). It was purified by n-hexane/benzene mixture.

Antimicrobial activity

Antimicrobial activity of chemically derived compounds was studied. Three bacterial and fungal strains were selected for the primary screening.

Microorganisms used

Clinical laboratory bacterial isolates of *Bacillus subtilis*, *Staphylococcus aureus*, and *Escherichia coli* and *fungal isolates viz., Fusarium oxysporium, Trichoderma reesei*

and *Penicillium funiculosum* were collected from the stock cultures of Microbiology Laboratory, SMS Medical College Jaipur, India.

Preparation of samples

The 10 mg/ml of samples was dissolved in DMSO and further dilutions were made for calculating *MIC* value.

Culture and maintenance of bacteria

Pure cultures obtained from SMS Medical College Jaipur, India were used as indicator organisms. These bacteria were grown in Nutrient agar medium (prepared by autoclaving 8 % Nutrient agar of Difco-Laboratories, Detroit, USA, in distilled water at 15 lbs psi for 30 min) by incubating at 37 ^{o}C for 48 h. Each bacterial culture was further maintained on the same medium after every 48 h of transferring. A fresh suspension of test organism in saline solution was prepared from a freshly grown agar slant before antimicrobial assay.

Determination of Antibacterial Assay

In vitro antibacterial activity of the samples was studied against gram positive and gram negative bacterial strains by the agar well diffusion method [32]. Streptomycin was used as reference antibacterial agent (control). Mueller Hinton agar no. 2 (Hi Media, India) was used as the bacteriological medium. The Mueller Hinton agar was melted and cooled to 48-50 ºC and a standardized inoculum (1.5×108 CFU/ml, 0.5 McFarland) was then added aseptically to the molten agar and poured into sterile petri dishes to obtain a solid medium. Wells were prepared in the seeded agar plates. The test compound (100 µl) was introduced in the well (6 mm). The plates were incubated overnight at 37 ºC. The antimicrobial spectrum of the chemical compounds was determined for the bacterial species in terms of zone sizes around each well. The diameters of zone of inhibition produced by the agent were compared with those produced by the commercial control antibiotics, streptomycin. For each bacterial strain controls were maintained where pure solvents were used instead of the chemical compound. The control zones were subtracted from the test zones and the resulting zone diameter was measured with antibiotic zone reader to nearest mm. The experiment was performed three times to minimize the error and the mean values are presented.

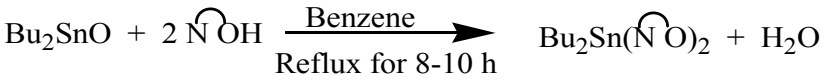
Determination of Antifungal Assay

Anti-fungal activity of the experimental plant was investigated by agar well diffusion method [33]. Ketokenazole was used as reference antifungal agent. The yeasts and saprophytic fungi were sub cultured on to Sabouraud's dextrose agar, SDA (Merck, Germany) and respectively incubated at 37 °C for 24 h and 25

°C for 2-5 days. Suspensions of fungal spores were prepared in sterile PBS and adjusted to a concentration of 106cells/ml. The plates were dried at room temperature for 15 min. Wells of 10 mm in diameter and about 7 mm apart were punctured in the culture media using sterile glass tube. 0.1 ml of several dilutions of fresh extracts was administered to fullness for each well. Plates were incubated at 37 °C. After incubation of 24 h bioactivities were determined by measuring the diameter of inhibition zone (in mm). All experiments were made in triplicate and means were calculated.

Results and discussion

The condensation reaction of carbohydrazide with suitable carbonyls in 1:1:1 molar ratio yields carbohydrazones. Sn(IV) complexes of carbohydrazones have been synthesized by the reaction of dibutyltin oxide with carbohydrazones in 1:2 molar ratio, in refluxing dry benzene gave corresponding coordination compounds of Sn(IV). These proceed with the liberation of water which azeotropicaly was removed as given below (Scheme 1).



Scheme 1. Synthetic route for the preparation of tin(IV) complexes.

All these prepared compounds are coloured viscous liquid and monomeric in nature. The purity of these compounds was checked by TLC using silica gel-G as adsorbent in DMF as the solvent. Conductivity measurement in DMF as solvent, showed a non-conductive behavior of these complexes due to no counter ion in the proposed structure of the complexes (15.4-25.3 $ohm^{-1}cm^2mol^{-1}$). The analytical data of carbohydrazones and their metal complexes are given at table 1, in a satisfactory agreement with the calculated values.

UV-Vis spectra

Most detailed information about the electronic structure of a compound, obtain by UV-Vis spectra. The UV-Vis spectra of the free ligands and their complexes were recorded using ethanol at room temperature. The UV spectrum of carbohydrazones (LH) showed two intense bands at 230-285 nm and 380-405 nm which belong to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transition respectively (table 2). In spectra of Sn(IV) complexes, the band at 230-285 nm attributed to $\pi\rightarrow\pi^*$ transitions are shifted towards the lower energy region (250-300 nm), which should be the result of the coordination of carbohydrazone ligand to the tin center. The band observed at 380-405 nm for free ligands is shifted to 345-380 nm in complexes due to coordination of azomethine nitrogen to the tin atom [34].

Table 2. UV-Vis Spectra of (HL) and their metal complexes.

Cmpd.	UV-Vis bands (nm)	Complexes	UV-Vis bands (nm)
L^1H	230, 380	A_1	250, 345
L^2H	238, 387	A_2	265, 357
L^3H	265, 392	A_3	290, 365
L^4H	255, 400	A_4	275, 375
L^5H	285,405	A_5	300, 380

Infrared Spectroscopic Study

The reaction of carbohydrazide with suitable carbonyls produced carbohydrazones (LH). This reaction was followed by disappearance of absorption bands at (3415-3450) cm-1 due to νOH of phenolic group and appearance of a characteristic new band in the range 1600-1625 cm-1 which is due to frequency of the free azomethine groups, νC=N are utilized to confirm the structures of (LH) [35-36]. This band splits into two sharp bands at 1615 cm-1 and 1595 cm-1 on complexation of azomethine nitrogen to tin ion whereas the other one is due to uncoordinated nitrogen of azomethine group. The bands due to νC=N were shifted to lower frequencies indicates the involvement of this group in bonding [37]. The medium to sharp intensity bands are observed around 525-540 cm-1 and 575-595 cm-1, which may be assigned to the asymmetric and symmetric mode [38] of νSn-C stretching vibrations in the spectra of tin complexes and also two bands at 525-550 cm-1 and 410-440 cm-1 may be assigned to νSn-O and νSn←N vibrations, respectively, indicating the participation of azomethine and phenolic oxygen in complexation [39-40]. The νC-O and ν(N-N) medium to strong intensity bands appear at 1260-1270 cm-1 and 985-995 cm-1respectively, these bands are also slightly shifted to higher frequency region as a result of complex formation, showing chelation of oxygen atom to the tin atom. IR spectral data are systemized at table 3.

Table 3. Characteristic stretching vibration frequencies (cm^{-1}) located at FT-IR oh (LH) and their metal complexes.

Compd.	$\nu_{C=N}$	ν_{Sn-N}	ν_{Sn-O}	ν_{N-N}	ν_{OH}
L^1H	1600	-	-	985	3425-3450
L^2H	1615	-	-	987	3420-3440
L^3H	1620	-	-	991	3415-3435
L^4H	1625	-	-	993	3417-3430
L^5H	1610	-	-	995	3422-3445
A_1	1572	415	545	997	-
A_2	1585	425	540	999	-
A_3	1580	430	550	1010	-
A_4	1592	440	535	1005	-
A_5	1595	410	525	1002	-

^{1}H NMR

The ^{1}H NMR data of ligands and their organotin(IV) complexes have been recorded in $CDCl_3$ (Table 4). In the ^{1}H NMR spectra of ligands, the signal due to the OH proton of the ligands appears at δ ~11.10-12.50 ppm (S), shifts downfield in the spectra of the corresponding tin complexes showing thereby chelation of the ligand moiety through the phenolic oxygen to the tin atom (δ ~ 11.35-12.95 ppm). In the case of the ligands, the proton signal for the methyl protons [-C(CH_3)=N] and azomethine protons [-CH=N] in the region δ ~ 1.75-1.85 ppm (S) and δ ~8.15-8.35 ppm, shifts downfield in the spectra of corresponding tin complexes on account of its deshielding, which is attributed to the donation of the lone pair of electrons by the azomethine nitrogen to the tin atom. The ligands show a complex multiplet in the region δ ~ 6.10-7.55 ppm for the aromatic protons which remains at almost the same position in the same spectra of the organotin(IV) complexes. However, a broad signal at δ ~ 3.25-3.75 ppm for the NH_2 protons remains almost unaltered in the tin complexes which clearly shows that this group does not take part in the complexation reaction. The complexes, however, show additional signals at δ ~ 0.85-1.90 ppm owing to the protons of the butyl group.

Table 4. ^{1}H NMR data for the ligands and for their corresponding organotin(IV) complexes.

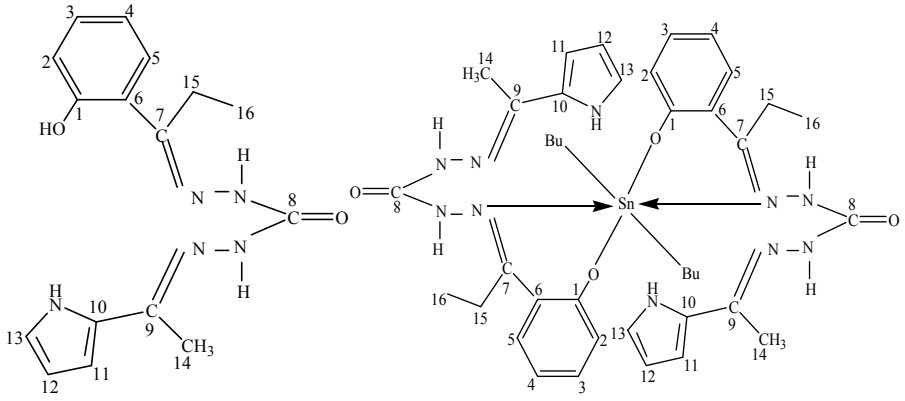
Comp. No.	-HCN	-OH	-CH_3CN	-NH_2	Aromatic protons
L^1H	8.20	11.10	1.75	3.30	6.15-7.20
L^2H	8.15	11.25	1.80	3.53	6.10-7.15
L^3H	8.35	12.50	1.85	3.77	6.65-7.34
L^4H	8.30	12.15	1.83	3.48	6.10-7.55
L^5H	8.25	11.55	1.79	3.40	6.78-7.35
A_1	8.65	11.35	1.88	3.35	7.25-7.80
A_2	9.12	11.45	1.90	3.60	7.15-7.75
A_3	9.25	12.95	2.00	3.80	7.68-7.95
A_4	9.02	12.50	1.97	3.56	7.35-7.89
A_5	9.08	12.10	1.95	3.48	7.45-7.87

^{13}C NMR Spectra

The ^{13}C NMR spectral data for carbohydrazones and its corresponding tin complexes are reported in Table 5. The shifting in the position of resonance of carbon attached to OH group suggests the bonding of oxygen to the tin atom. The signal due to the carbon atom attached to the azomethine group in the ligands appears at δ ~ 171.3-173.4 ppm. Further the shifting of azomethine (>C=N) carbon signal in the spectra of complexes (δ ~ 164.8-165.3 ppm) indicate that the azomethine nitrogen has been involved in coordination with the tin atom. The carbon of butyl group is observed at δ ~13.8-29.1 ppm which is comparable to other similar tin compounds [41].

Table 5. ^{13}C NMR data for the ligand and for its corresponding organotin(IV) complexes.

Compd.	Chemical shift value in δ ppm														
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16
L^1H	154.3	115.2	128.5	118.1	127.5	118.3	173.4	168.6	174.8	142.4	11.4	11.9	12.5	12.1	12.2	117
A_1	164.6	116.4	129.9	119.8	128.7	119.6	165.7	183.8	166.3	143.9	10.5	11.3	11.9	13.8	13.3	121



L^1H $[SnBu_2(L^1)_2]$

^{119}Sn NMR Spectra

^{119}Sn NMR spectra of tin complexes have been recorded using TMT (tetramethyltin) as external standard. Tin (IV) complexes give sharp signals at δ ~ -352.8 ppm, which is in accordance with the proposed six coordinated distorted octahedral geometry, in agreement with the previously reported values [42]. Chemical shift values for similar six coordinated Bu_2Sn(IV) complexes have been reported in the range of δ ~ -275.5 to -370.5 ppm.

In vitro antimicrobial assay

The *in-vitro* antibacterial activity of the ligands and their complexes were screened against three bacterial strains by well diffusion method using streptomycin as reference they showed significant potent activity. The susceptibility of bacterial strain toward the compounds was estimated by measuring the size of inhibition zone diameter. It is evident from the results that the antibacterial activity of some of the metal complexes is higher than the free ligands and lesser than the standard against all the bacteria tested. In case of antibacterial activity carbohydrazones and their metal complexes were found to be active. Antifungal activity of the ligands and their complexes were screened against three fungal strains by well diffusion method using ketokenazole as reference they showed some potent activity. The antimicrobial results are systemized at table 6. It is, however, known that the chelating

tends to make carbohydrazones act as more powerful and potent bacterostatic agents, thus, inhibiting the growth of bacteria and fungi more than the parent carbohydrazones.

Table 6. Antimicrobial results of carbohydrazones and their metal complexes.

Cmpd.	Antibacterial activity zone of inhibition (mm)					Antifungal activity zone of inhibition (mm)				
	Bacterial strain	20 ml	40 ml	60 ml	80 ml	Fungal strain	20 ml	40 ml	60 ml	80 ml
L^1H	*B. subtilis*	8	10	14	16	*F. oxysporium*	nill	nill	10	13
	S. aureus	11	12	14	17	*T. reesei*	nill	10	15	18
	E. coli	9	14	14	18	*P. funiculosum*	8	10	13	16
L^2H	*B. subtilis*	10	12	14	17	*F. oxysporium*	9	10	13	14
	S. aureus	11	13	16	18	*T. reesei*	8	10	14	15
	E. coli	9	11	14	16	*P. funiculosum*	9	12	14	16
L^3H	*B. subtilis*	8	11	13	15	*F. oxysporium*	nill	10	13	17
	S. aureus	10	12	14	17	*T. reesei*	8	9	11	13
	E. coli	9	12	14	16	*P. funiculosum*	9	12	14	16
L^4H	*B. subtilis*	9	10	12	14	*F. oxysporium*	8	11	12	13
	S. aureus	10	11	13	15	*T. reesei*	8	10	11	15
	E. coli	10	12	13	17	*P. funiculosum*	9	10	12	14
L^5H	*B. subtilis*	9	10	13	15	*F. oxysporium*	9	10	13	15
	S. aureus	10	12	14	16	*T. reesei*	8	9	12	14
	E. coli	11	12	14	15	*P. funiculosum*	nill	8	12	16
A_1	*B. subtilis*	12	13	14	16	*F. oxysporium*	10	12	14	nill
	S. aureus	12	14	15	19	*T. reesei*	nill	8	10	13
	E. coli	10	12	14	16	*P. funiculosum*	10	13	14	16
A_2	*B. subtilis*	10	13	16	18	*F. oxysporium*	10	12	14	16
	S. aureus	13	14	17	18	*T. reesei*	11	12	13	14
	E. coli	10	13	16	18	*P. funiculosum*	12	14	15	16
A_3	*B. subtilis*	10	11	14	16	*F. oxysporium*	8	12	13	16
	S. aureus	11	12	15	18	*T. reesei*	10	12	13	14
	E. coli	12	15	16	17	*P. funiculosum*	10	13	15	18
A_4	*B. subtilis*	10	12	13	16	*F. oxysporium*	10	13	15	16
	S. aureus	11	12	14	15	*T. reesei*	12	14	17	18
	E. coli	11	13	15	17	*P. funiculosum*	11	12	14	16
A_5	*B. subtilis*	11	13	15	19	*F. oxysporium*	10	12	13	17
	S. aureus	12	14	16	17	*T. reesei*	10	13	14	16
	E. coli	12	13	18	16	*P. funiculosum*	10	12	13	14

Streptomycin (for bacteria) – Inhibition zone – 20mm; Ketokenazole (for fungi) – Inhibition zone – 22mm. *Standered

Structure of Sn(IV) complexes [A^1-A^5]

On the basis of above spectral analysis, a shift in the position of O-H, C-O, N-N and –C=N groups suggest the bidentate nature of ligands. In all Sn(IV) complexes (Figure 1), in view of the presence of one bidentate chelate rings, three chlorine atoms, one butyl group and monomeric nature of these complexes, the following structure is being proposed in which central tin atom acquires distorted octahedral geometry.

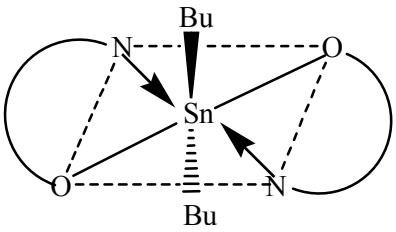


Figure 1. Sn(IV) complexes (A^1 – A^5).

Conclusion

In summary, we have synthesized some coordination compounds of tin(IV) with carbohydrazone ligands and determined their structure and physical properties. IR and NMR spectral studies suggest the bidentate nature of ligands, which coordinate with Sn(IV) ions through azomethine nitrogen and phenolic oxygen. The distorted octahedral geometry of these compounds of the type [$SnBu_2$(L)2] (where L = carbohydrazone ligand) have been proposed on the basis of elemental analysis, spectral studies *viz*., IR, UV-Vis and NMR (^{1}H,^{13}C and ^{119}Sn). These compounds show non electrolytic nature. Furthermore, these Sn(IV) complexes were found to have significant antibacterial and antifungal activity.

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References

[1] Shrivastav, N. K. Singh, P. Tripathi, T. George, J. R. Dimmock, R. K. Sharma, *Biochim*., 88, 1209 (2006).

[2] Z. H. Cohen, H. Pervaz, K. M. Khan, C. T. Supuran, *J. Enzyme Inhib. Med. Chem*., 20, 81 (2005).

[3] H. J. Cristau, P. P. Cellicer, J. F. Spindler, Eur. *J. Org. Chem*., 4, 695 (2004).

[4] J. R. Dimmock, P. Kumar, T. M. Allen, G. Y. Kao,S. Halleran, J. Balzarini, E. de Clercq, *Phramazie*, 52, 182 (1997).

[5] G. M. Abu El-Reash, O. A. El Gammal, A. H. Radwan, *Spectrochim. Acta Part A: Mol. Biomol.Spectrosc*., 121, 259 (2014).

[6] N. W. Ahmad, S. A. Mohd, S. Balabaskaran, V. G. Das, Kumar, *Appl. Organomet. Chem*., 7, 583 (1993).

[7] M. F. Mohon, K. C. Molloy, P. C. Waterfield, *J. Organomet. Chem*., 361, C5 (1989).

[8] M. Gielen, M. Biesemans, D. de Vos,

Willem, *J. Inorg. Biochem*., 79, 139 (2000).
[9] Kizlink, J. Chem. *Listry*, 86, 178 (1992).
[10] A. Fredriksson, G. Nestor, B. H. Sevensson, *Vatler*, 59, 271 (2003).
[11] W. Rehman, A. Badshah, S. Khan, L.T. Anh Tuyet, *Eur. J. Med. Chem*., 44, 3981 (2009).
[12] P. N. Saxena, A. Crowe, *J. Appl. Organomet. Chem.,* 2, 185 (1998).
[13] C. J. Evans, S. Karpel, *J. Organomet. Chem.*, 1, 16 (1985).
[14] M. Mohan, A. Agrawal, N. Jha, *J. Inorg. Biochem.*, 34, 41 (1981).
[15] P. Quevauviller, R. Ritsema, R. Morabit, W. M. R. Dirkx, *Appl. Organomet. Chem*., 541, 8 (1994).
[16] L. L. Liu, J. T. Wang, N. Chungkuo, M. Leu, P. M. Meng, *Pallet Bull*., 63, 535 (2011).
[17] M. Sonmez, M. Celebi, I. Berber, *Eur. J.* Med. Chem., 45 1935 (2010).
[18] H. F. A. El-halm, M. M. Omar, G. G. Mohammed, *Spectrochim Acta, part A*, 78, 36 (2011).
[19] G. G. Mohammed, M. A. Zayed, S. M. Adallah, *J. Mol. Struct.,* 979, 62 (2010).
[20] I. Sakiyan, E. Logoglu, S. Arslan, N. Sari, N. Sakiyan, *Biomet*., 17, 115 (2004).
[21] Z. H. Chohan, M. Hassan, K. M. Khan, C. T. Supuran, *J. Enz. Inhib. Med. Chem.,* 20, 183 (2005).
[22] A. P. Rebolledo, G. M. de lima, L. N. Gumbi, N. L. Speziali, D. F. Maia, C. B. Pinheiro, J. D. Ardisson, M. E. Cortes, H. Beraldo, *Appl. Organomet. Chem*., 17, 945 (2003).
[23] S. Belwal, R. K. Saini, R. V. Singh, *Indian J. Chem.,* 37A, 245 (1998).
[24] N. K. Singh, A. Srivastava, A. Sodhi, P. Ranjan, *Transit. Metal Chem*., 25, 133 (2000).
[25] T. D. Thangadurai, K. Natrajan, *Transit. Metal Chem*., 26, 717 (2001).
[26] A. Crowe, *J. Appl. Organomet. Chem*., 1, 143 (1987).
[27] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, Sixth Ed., Wiely India Edition (Wiely Student Edition), (1297).
[28] R. Wleilm, A. Bouhdid, M. Biesemans, J. C. Martins, D. de Vos, E. R. T. Tiekink, M. Gielen, *J. Organomet. Chem*., 514, 203 (1996).
[29] H. L. Singh, M. K. Gupta, A. K. Varshney, *Res. Chem. Intermed*., 27, 605 (2001).
[30] D. D. Perrin, W. L. F. Armarago, D. R. Perrin, Purification of Laboratory Chemicals, Second Ed., Pergamon Press, New York, (1980).
[31] G. M. Abu El-Reash, O. A. El Gammal, S. E. Ghzay, A. H. Radwan, *Spectrochim. Acta Part A: Mol. Biomol*. *Spectrosc*., 104, 26 (2013).
[32] C. Perz, M. Paul, P. Bazerque, *Biol. Med. Exp.,* 15, 113 (1990).
[33] S. Bonjar, S. Aghighi, N. A. Karimi, J. Biol. Sci., 4, 405 (2005).
[34] M. K.Gupta, H. L. Singh, S. Varshney, A. K. Varshney, Bioinorg. *Chem. and App*., 1,

309 (2003).

[35] Jayabala Krishnan, C. Natarajan, *Synth. React. Org. Met.-Org. Chem*., 31, 983 (2001).

[36] R. Ramesh, N. Dharmaraj, R. Karvembu, K. Natrajan, *Ind. J. Chem*., 39, 1079 (2011).

[37] K. Nakamoto, *Infrared of Inorganic and Coordination Compounds*, Sixth Ed., John-Wiely, Inc., New York, London, (1997).

[38] N. S. Biradar, V. H. Kulkarni, J. Inorg. Nucl. Chem., 33, 2451 (1971).

[39] W. D. Honnick, J. J. Zuckerman, *J. Organomet. Chem.,* 178, 133 (1979).

[40] P. Jain, K. K. Caturvedi, *J. Indian Chem*. Soc., 52, 805 (1975).

[41] H. L. Singh, M. Sharma, A. K. Varshney, *Synth. React. Met.-Org.Chem*., 29, 817 (1999).

[42] K. C. Molloy, P. C. Waterfield, *J. Organomet. Chem*., 424, 281 (1992).