Research Paper Medical Science

Synthesis,Spectral,Thermal and Antimicrobial Assay of Six Co-ordinate Complex and Heterocyclic Base Adducts of Zn (II) Derived from Thiosemicarbazone Moiety

Dr. J. R. Gujarathi | Pratap College, Amalner (M.S.)

ABSTRACT

Adducts of zinc (II) complex have been synthesized by the reaction of zinc (II) chloride with 5-chloro-2-hydroxy acetophenone thiosemicarbazone in presence of heterocyclic base like pyridine (py), α -picoline. Thiosemcarbazone has been characterized by 13C, 1H NMR,ESI-MS as well as IR, electronic spectra.Spectral and magnetic measurements indicated Octahedral geometry for the six coordinate. The thiosemicarbazone and its Zn (II) complexes have been found antifungal,antibacterial and show growth inhibitory activity against Citrobactor, Acinetobactor Aspergillus Niger and Candida Albicans.

KEYWORDS Thiosemicarbazone, metal salts,Bioactive metal complexes, antimicrobial activity.

Introduction

Thiosemicarbazones are good ligands with beneficial biological activity.Their biological activity is related to ability to coordinate to metal centres.Thiosemicarbazone derivatives possess additional functional groups which can coordinate to metal ion.This suggests the biological activity may also depend on the non coordinating groups.

Thiosemicarbazones are the derivatives of thiourea. The study of their chemical and structural properties is important due to the wide application in the chemotherapeutic field [1, 3]. Thiosemicarbazones form complexes with many metals. These complexes are of diverse chemical, physical and structural characteristics [1, 2]. Thiosemicarbazones, usually react as chelating ligands with transition metal ions by bonding through the sulfur and hydrazinic nitrogen atom. The group N—-C=S is responsible for the pharmacological activity. Thiosemicarbazones of or-(N)-heterocyclic aldehydes and ketones possess chemotherapeutic activities such as antimalarial, antibacterial, antiviral activities [4,5].

Thiosemicarbazones constitute nitrogen, sulfur donor atoms because of important chemical, biological and medicinal properties [1,6]. The coordination chemistry of ONS donor ligands is of interest due to their structural and biological properties[7, 8]. The biological activity of certain thiosemicarbazones is because of their ability to form complexes with transition metal ions bonding through oxygen ,nitrogen and sulfur atoms (ONS).But in some cases, decrease of activity is due to lowering of the thiosemicarbazone's denticity [6]. Salicylaldehyde thiosemicarbazone is a tridentate (ONS donar) ligand capable of stabilizing both higher and lower oxidation states of transition metal ions [9-13].It acts as dianionic ligand on deprotonation at both the phenol and thioamide functions. It can also act as monoanionic chelating ligand, coordinating to a metal ion through the deprotonated phenolic oxygen, the thione sulfur and the azomethine nitrogen [9]. The dianionic form of the ligand is favoured at higher pH, whereas the monoanionic form is at low pH.

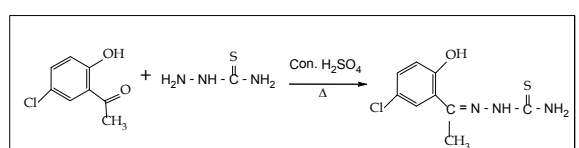
Zinc (II) complexes of carboxylates appeared to have good antibacterial activity. A strong inhibitive effect was observed towards *E. coli* and *S. aureus* [14].The interaction between zinc and the gyrase inhibitor ciprofloxacin and various nitrogen-donor ligands have been studied and the complexes were found more potent than the drugs alone [15].The complexes of thiosemicarbazones with Zn (II) gave good results. A selective activity was observed by Zn(II) complexes of picolinaldehyde-*S*-methyl- and -*S*-benzylthiosemicarbazones which found active in comparison to free ligands [16].Zn(II) complexes with sulfadrugs, also proved effective antifungal agents against *Aspergillus* and *Candida* species. Moreover, the activities of the complexes were found higher than the free ligands and lower than the drug ketoconazole [17]. Zn (II) complexes showed very good inhibitory activity against yeast *Candida albicans* [18].

In the present work the synthesis, spectral characterisation and biological studies of six coordinate complexes of zinc (II) with 5-chloro 2-hydroxy acetophenone thisemicarbazone have been reported.

Experimental

Materials and instrumentation

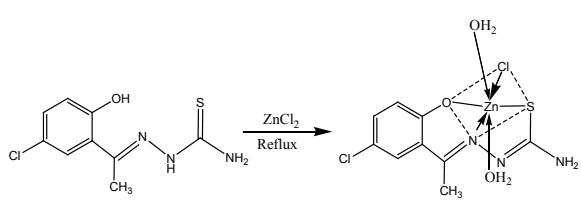
The thiosemicarbazone was synthesized by refluxing 5-chloro 2-hydroxy acetophenone and thiosemicarbazide in ethanol in the mole ratio 1:1 for 3 hours. The pale yellow product obtained was filtered and washed with cold ethanol and then diethyl ether. It was recrystalised by hot ethanol and dried over P_2O_5 in vacuum.



SCHEME - I

Preparation of complex

Zn (II) salt was dissolved in absolute ethanol.The ethanolic solution of thiosemicarbazone in slight excess over the metal:ligand ratio of 1:1 was added to it dropwise and with constant stirring.The rection mixture was refluxed for an hour on a hot water bath.The light yellow product thus obtained was fitered and washed well with absolute ethanol and then diethyl ether and dried over P_2O_5 in vacuum.

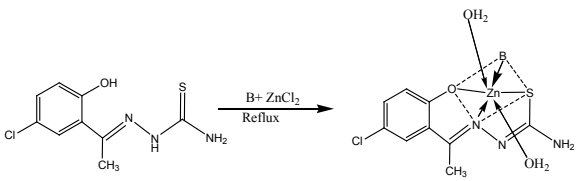


Scheme II

Preparation of adducts

The complex Zn.L.B (B is heterocyclic base like pyridine, α-picoline, β-picoline,γ-picoline) was synthesized by adding slowly ehanolic solution of $ZnCl_2$,heterocyclic base to the hot ehanolic solution of ligand in the ratio 1:1:1 and refluxing re-

action mixture for one hour. The yellow adduct obtained was filtered and washed with hot water, cold ethanol and diethyl ether and dried over P_2O_5 in vacuum.



Scheme III

(B= pyridine,α-picoline,β-picoline,γ-picoline)

Physical measurements-

Magnetic moments were measured by Faraday method. IR spectra were recorded in the range 4000-200 cm^{-1} range. NMR spectra were recorded in the mixture of $CDCl_3$ and DMSO-d_6 (1:1 v/v) with a Bruker AC-300F 300MHz spectrometer. Conductivity measurements were carried out on conductivity Bridge, Systonics conductivity meter-304. Thermo gravimetric analysis was carried out in the temp rnge 28-800°C. UV-Visible spectra were measured on Jasco UV-visible double beam spectrophotometer.Metal in the complex and adducts was estimated by standerdized E.D.T.A using Erichrome black-T as an indicator.Chloride in the complex was determined by Mohr's method.

Table 1 Physical properties:

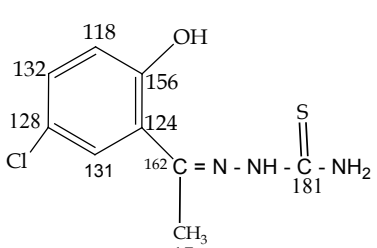
Compounds	Colour	Empirical Formula	Molar conductance $Ohm^{-1}cm^{-2}mole^{-1}$	Magnetic Moment B.M.
L	Yellow	$C_9H_{10}ClN_3OS$	-	-
Zn-L.Cl.$(H_2O)_2$	Yellow	$C_9H_{12}N_3O_3Cl_2SZn$	30.5	Diamagnetic
Zn.L.Py.$(H_2O)_2$	Yellow	$C_{14}H_{17}N_4O_3ClSZn$	28.6	Diamagnetic
Zn.α-Pico.$(H_2O)_2$	Yellow	$C_{15}H_{19}N_4O_3ClSZn$	25.7	Diamagnetic
Zn.L β-Pico.$(H_2O)_2$	Yellow	$C_{15}H_{19}N_4O_3ClSZn$	20.4	Diamagnetic
Zn.L.γ-Pico.$(H_2O)_2$	Yellow	$C_{15}H_{19}N_4O_3ClSZn$	33.3	Diamagnetic

^{1}H-NMR

NMR signals at 12.00, 2.25 ppm are assigned to – OH, - CH_3 protons respectively.

No peak is observed corresponding to S-H proton, indicating it exists in thioketo form. ^{4}NH shows litte low field position (8.20 ppm) could be due to the deshielding caused by – N = C〈 of the system N=CSH = NH. Signal at 11.5 ppm is due to ^{2}NH. Aromatic protons show multiplets at 6.9, 7.25 and 7.60 ppm.

^{13}C-NMR (DMSO-D_6): δppm 118 (C = C), 132 (C = C), 128 (C = C – Cl), 131 (C = C), 124 (C = C), 156 (C = C – OH), 162 (C = N), 181 (C=S), 17 (C-CH_3).



(Calcd) found ESI-MS m/z, ion M$^+$: $C_9H_{10}ClN_3OS$ (243.70) 243.02, $C_9H_{12}N_3O_3Cl_2SZn$ (362.56) 362.11, $C_{14}H_{17}N_4O_3ClSZn$ (422.15) 422.92, $C_{15}H_{19}N_4O_3ClSZn$ (436.24) 436.88, $C_{15}H_{19}N_4O_3ClSZn$ (436.24) 436.69, $C_{15}H_{19}N_4O_3ClSZn$ (436.24) 436.91.

Analytical data

1.**L:** % C 44.07 (44.35),% H 4.81 (4.14),% N 17.92 (17.24),% S 13.91 (13.16)

2. **Zn-L.Cl.$(H_2O)_2$:** % Zn 18.12 (18.04), %Cl 9.27 (9.78), %C 29.12 (29.81), %H 3.89

(3.34), %N 11.07 (11.59), %S 8.12 (8.84).

3**. Zn.L.Py.$(H_2O)_2$:** % Zn 15.70 (15.49), %C 39.04 (39.83), %H 4.83 (4.06), %N 13.72

(13.27), %S 7.10 (7.59).

4.**Zn.α-Pico.$(H_2O)_2$**: % Zn 14.25 (14.99), %C 41.70 (41.30), %H 4.84 (4.39), %N 12.14

(12.84), %S 7.88 (7.35).

5. **Zn.L β-Pico.$(H_2O)_2$**: % Zn 14.20 (14.99), %C 41.84 (41.30), %H 4.80 (4.39), %N 12.10

(12.84), %S 7.82 (7.35).

6. **Zn.L.γ-Pico.$(H_2O)_2$**: % Zn 14.20 (14.99), %C 41.72 (41.30), %H 4.80 (4.39), %N 12.12

(12.84), %S 7.89 (7.35).

Table 2 .Electronic spectral data (cm^{-1})

Compound	Mode	MLCT	n→π*	π→π*
L	DMF	-	30971	35865
Zn-L.Cl.$(H_2O)_2$	DMF	25641	32465	34889
Zn.L.Py.$(H_2O)_2$	DMF	25641	31156	34444
Zn.α-Pico.$(H_2O)_2$	DMF	25641	32580	34553
Zn.L β-Pico.$(H_2O)_2$	DMF	25907	32110	34478
Zn.L.γ-Pico.$(H_2O)_2$	DMF	25500	32650	34667

Infrared Spectroscopic data (cm^{-1})

1.**L**: ν (- OH) 3310; ν (C = N) 1630; ν (- C = S) 788, 1365 ; ν (N – N) 1058; ν (^{2}N-H) 3235; ν (C – O) 1287.

2 [Zn-L.Cl.$(H_2O)_2$**]:** ν (C = N) 1610; ν (C = N-N=C) 1542, ν (C-S) 701, 1310,ν (N-N) 1118, ν(M - N) 450, ν (M-O) 522, ν (M-S) 319, ν (C - O) 1222, ν(H_2O) 3510,3548.

3.[Zn.L.Py.$(H_2O)_2$**]:** ν (C = N) 1599; ν (C = N-N=C) 1535, ν (C-S) 710, 1312; ν (N-N) 1122, ν (M - N) Base 270, ν (M - N) 455, ν (M - O) 529, ν (M-S) 312, ν (C - O) 1229, Band due to HB 1465, ν(H_2O) 3545,3565.

4.[Zn.α-Pico.$(H_2O)_2$**]:** ν (C = N) 1597; ν (C = N-N=C) 1518, ν(C-S) 712, 1318, ν (N-N) 1121, ν (M - N) Base 275, ν (M - N) 452, ν (M - O) 526, ν (M-S) 315, ν (C - O) 1230, Band due to HB 1460, ν(H_2O) 3548,3571.

5.[Zn.L β-Pico.$(H_2O)_2$**]:** ν (C = N) 1602; ν (C = N-N=C) 1514, ν (C-S) 717, 1304,ν (N-N) 1120, ν (M - N) Base 278, ν (M - N) 458, ν (M - O) 530, ν (M-S) 318, ν (C - O) 1232, Band due to HB 1470, ν(H_2O) 3551,3575.

6.[Zn.L.γ-Pico.$(H_2O)_2$**]:** ν (C = N) 1605; ν (C = N-N=C) 1517, ν (C-S) 719, 1312,ν (N-N) 1121, ν (M - N) Base 272, ν (M - N) 452, ν (M - O) 536, ν (M-S) 312, ν (C - O) 1234, Bands due to

HB 1464, ν(H_2O) 3558,3580.

TGA analysis data:
The TGA curves of complexes were recorded between the temperatures 30 °C to 800 °C

1. **[**Zn-L.Cl.(H_2O)$_2$**]**: First step, 115.5 °C, Mass loss 4.98 % second step, 130.29 °C, Mass loss, 9.95 % Third Step 245.43 °C, Mass loss, 30.02 % Fourth Step, 370.14 °C, Mass loss 60.5 %, Residue 800 °C, % of ZnO, 22.96 (22.45).
2. **[**Zn.L.Py.(H_2O)$_2$**]:**First step, 115 °C, Mass loss 4.28 % second step,131.40 °C, Mass loss, 8.55 % Third Step 250 °C, Mass loss, 32.02 % Fourth Step, 369.30 °C, Mass loss, 60.01 %, Residue, 792.34 °C, % of ZnO, 19.72 (19.28).
3. **[**Zn.α-Pico.(H_2O)$_2$**]:** First step, 115.35 °C, Mass loss 4.15 % second step, 130.50 °C, Mass loss, 8.26 % Third Step 249.40 °C, Mass loss, 30.47 % Fourth Step, 365.15 °C, Mass loss 62.5 %, Residue 800 °C, % of ZnO, 18.02 (18.66).
4. **[**Zn.L β-Pico.(H_2O)$_2$**]:**First step, 115.26 °C, Mass loss 4.17 % second step, 132.14 °C, Mass loss, 8.27 % Third Step 250 °C, Mass loss, 29.02 % Fourth Step, 366.35 °C, Mass loss, 65.27 %, Residue, 779.50 °C, % of ZnO, 18.10 (18.66).
5. **[**Zn.L.γ-Pico.(H_2O)$_2$**]:**First step, 114.92 °C, Mass loss 4.16 % second step, 131.20 °C, Mass loss, 8.25 % Third Step 245.43 °C, Mass loss, 33.28 % Fourth Step, 370.28 °C, Mass loss 60.78 %, Residue 800 °C, % of ZnO, 18.12 (18.66).

Antimicrobial Assay (Agar well diffusion method)
Table.3 % Activity index of L , Zn (II) complexes and standered

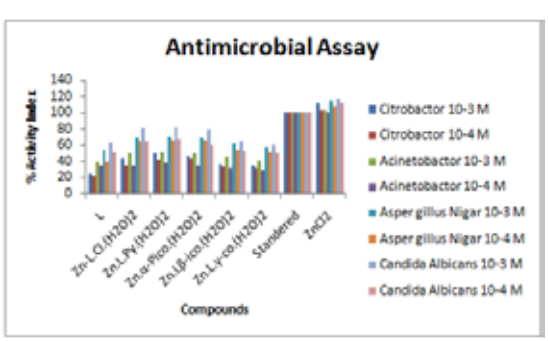
Compound % Activity Index	Citrobactor		Acinetobactor		Asper gillus Nigar		Candida Albicans	
	10^{-3} M	10^{-4} M	10^{-3} M	10^{-4} M	10^{-3} M	10^{-4} M	10^{-3} M	10^{-4} M
L	25.12	22.37	40.18	35.31	54.60	40.32	63.67	51.03
Zn-L. Cl.(H_2O)$_2$	44.10	35.17	50.02	35.60	69.22	65.22	81.32	65.11
Zn.L.Py. (H_2O)$_2$	49.37	42.42	51.02	37.70	70.21	66.19	82.35	67.12
Zn.α-Pico. (H_2O)$_2$	47.06	43.68	50.58	35.40	69.24	65.74	79.10	61.10
Zn.Lβ-ico. (H_2O)$_2$	37.20	33.39	45.24	32.42	62.61	53.91	65.35	52.34
Zn.L.γ-co. (H_2O)$_2$	35.15	32.11	41.14	30.12	58.12	51.12	60.41	50.00
Standered	100	100	100	100	100	100	100	100
$ZnCl_2$	112.5	102.57	103.35	100.32	114.22	108.08	116.33	112.23

(Standered -Cefodoxine,Fluconazole)

% activity index was calculated by the formula

$$\% \text{ Activity Index} = \frac{\text{Zone of inhibition of test compound}}{\text{Zone of inhibition of standard (diameter)}} x100$$

Fig 1 Antimicrobial Assay



Results and discussion
Physica data of ligand and its complexes are presented in Table 1. Elemental analysis data confirmed with 1:1 ratio of metal ion, thiosemicarbazone for complex and 1:1:1 ratio for metal, thiosemicarbazone and heterocyclic base for all adducts. The complex and all adducts are soluble in DMF in which conductivity measurements were made (30^{0}C), showing all complexes to be non electrolyte [19].The magnetic moments were measured at room temperature (27^{0}C) in polycrystalline state showed diamagnetic behavior expected for d^{10} configuration. Mass spectral data confirmed the structure of the thiosemicarbazone as indicated by molecular ion peak (M + 1) corresponding to their molecular weights. UV-visible spectra of metal complexes in DMF solution are presented in Table no.2 The thiosemicarbazone has band π- π*band [20-22] at 35,865 cm^{-1} and n- π*[23,24] at 30,971 cm^{-1}. There is no absorption bands occurred above 500 nm in DMF solution indicating the absence of d-d transition bands. These bands are slightly shifted to higher energy side in complexes. The π-π*absorption bands are shifted to longer wavelength in complexes due to the weakening of the C=S bond conjugation system gets enhanced on complexation [25,26].The reduction in intensity of n- π*bands in the complexes is due to transfer of lone pair of electrons to the metal and coordination of azomethine nitrogen. MLCT bands are broad in the complexes and observed in the region 25000-26000 cm^{-1} which are assignable to Zn→S transitions.

The absence of any band in 2600-2800 cm^{-1} region of the IR spectrum of thiosemicarbazone complex shows the absence of thiol tautomer in the solid state. Coordination of the azomethine nitrogen ^{7}C=N^1 shift the frequency to the lower side [27] A new bandin the range 450-460 cm^{-1} confirms the coordination of azomethine nitrogen [28,29]. The increase in frequency of ^{1}N-^{2}N is due to the increase in double bond character offsets the loss of electron density via donation to the metal. This confirms the coordination of the ligand through the azomethine nitrogen atom. The band ^{2}N-H of thiosemicarbazone disappears in the complexes indicating the deprotonation of the ^{2}N-H proton. A thioamide band which is partly due to C=S found at 1365 and 788cm^{-1} in thiosemicarbazone shifted to lower side in complexes indicating coordination through thiolate sulfur [30]. A new band in 310-320 range due to Zn-S is another indication of the involvement of sulfur coordination. The phenolic oxygen occupies the third coordination on loss of OH protons. These causes of shifting of ν(CO) 1287 cm^{-1}in uncomplexed thiosemicarbazone to lower side in the complexes. The new bands due to Zn-O in complexes in the range 520-540 cm^{-1} confirm coordination through oxygen. The heterocyclic base nitrogen atom occupies fourth coordination site. The band is assigned for ν (Zn-N) due to heterocyclic base in 260-275 cm^{-1} range in the spectra of all complexes. The characteristics bands of coordinated heterocyclic bases are also observed in IR spectra of all complexes [31-33].

The TGA curves of Zn (II) complex and adducts were recorded within a temperature range 30-800^{0}C. The data indicated that the decomposition of complex proceed in four steps. Hydrations of water molecules were lost in between 30-110^{0}C. The two coordinated water molecules were lost in the temperature range 114-116^{0}C.At this stage corresponding mass loss is about 4-5 %. No change is seen up to ~ 130^{0}C after that there is break in the curves due to evaporation of molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 600^{0}C. Finally the metal oxides were formed above 600^{0}C. The decomposition was complete at ~ 800^{0}C.

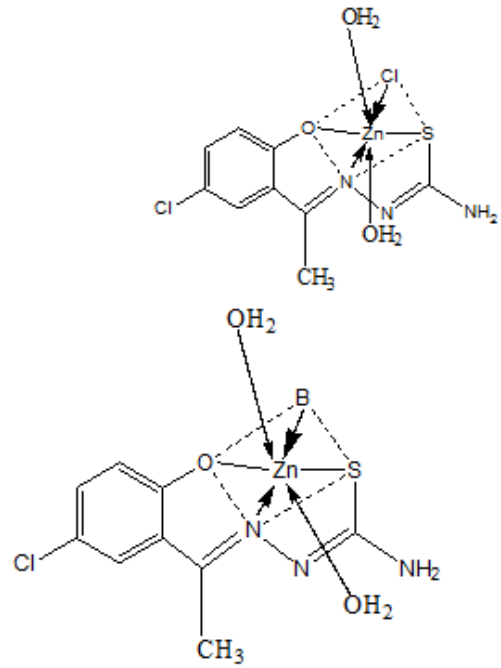
It has been found that Zn (II) complex and adducts were stable up to 114^{0}C and decomposition started at this temperature. The second step temperatures are in the range of 130-132^{0}C. The third step temperatures are in the range of 240-250^{0}C. The solid residue is ZnO . The complexes prepared with different metals decompose in steps. It is evaluated that the coordination of metal ion to ligand is responsible for the thermal stabilities of metal complexes [34].

The antibacterial activity was determined using the agar well diffusion method. The activity was determined by measuring the diameter of the inhibition zone (in mm) showing by the hanging drop method. Biological activity was measured in two different molar concentrations (10^{-3}M, 10^{-4} M). The chelate Zn.L.py $(H2O)_2$ showed maximum activity against bacterial and fungal species than free ligand. The results of antibacterial and antifungal studies are given in Table 3.The thiosemicarbazone was found less active than its zinc complex and adducts. The most probable reason for this difference might be due to chelation which reduces the polarity of the central metal atom because of the partial sharing of its positive charge with donor groups and possible π-electron delocalisation within the whole chelating ring. As a result of this, the lipophilic nature of the central metal atom increases, which favours the permeation of the complexes through the lipid layer of the cell membrane[35].Thus increase in coordination number increases microbial activity.*Acinetobactor* and *Citrobactor* are gram –ve bacterial species. In gram negative bacteria the outer membrane is thinne and they possess outer membrane. So, it might not be easy for the complexes to diffuse inside the bacterial cell. A very good inhibitory activity was also found by the yeast *Candida albicans* [36]. The metal chloride salts were more effective than complexes. This shows that free metal ions are more effective than one bound in complexes.But use of metal ion solution to treat bacterial diseases is toxic,so it can be used in coordinated form with ligand. The general sequence of % activity index can be represented as -

Standard > metal salt > complexes > ligand.

The % activity index decreases on dilution ie it is more in concentrated solution.

Expected structure



(B = pyridine, α-picoline, β-picoline,γ-picoline)

REFERENCES

1Campbell . J.M. Coord. Chem. Rev. 15 1975 279. | 2.. Padhye G.B. Kauffman, Coord. Chem. Rev. 63 (1985) 127. | 3. D.X. West, S.B. Padhye, P.B. Sonawane, Struct. Bonding (Berlin) 76 (1991) | 4. Klayman D.L. Hoch J.M, Scovill J.P Lambross C. Dobeek A.S. J.Pharm. Sci. 73 1984 1763. | 5. Dodd R.H. Quannes C. Robert Gero M, Potier P. J. Med. Chem. 32 1989 1272. | 6. West D.X. Padhye S.B. Sonawane P.B. Struct. Bonding, Springer,Heidelberg 76 1991 1. | 7. Casas J.S, Garcia-Tasenda M.S, Sordo J. Coord. Chem. Rev. 209 2000 197. | 8.John R.P, Sreekanth A, Kurup M.R.P Mobin S.M. Polyhedron 21 2002 2515. | 9.. Purohit S, Koley A.P, Prasad L.S,Manoharan P.T, Ghosh S. Inorg. Chem.28 1989 3735. | 10.. Koley A.P, Purohit S,Ghosh S, Prasad L.S, Manoharan P.T .J. Chem.Soc., Dalton Trans. 1988 2607. | 11. Leovac V.M, Petrovic A.F. Trans. Met. Chem. 8 1983 337. | 12.. Petrovic A.F, Vukadin M.L,Riber B. Trans. Met. Chem. 11 1986 207. | 13.. Koley A.P, Nimala R,Prasad L.S,Ghosh S,Manoharan P.T. Inorg. Chem.3l 1992 1764. | 14. Szunyogova E, Mudronova D, Gyoryova G, Nemcova R, Kovarova J, Piknova-Findorakova L. J. Therm. Anal. Calorim. 88, 2007 355. | 15. Patel M, Chhasatia M, Parmar P, Eur. J. Med. Chem. 45, 20104 39. | 16. Kizilcikli I.; Kurt Y.D.; Akkurt B.; Genel A.Y.; Birteksoz S.; Otuk G.; Ulkuseven BFolia Microbiol. 52, .2007 15. | 17 Mastrolorenzo A.; Scozzafava A.; Supuran C.T. Eur. J.Pharm. Sci. 11 2000 99. | 18. Mitic D,Milenkovic M, Milosavljevic S, Godevac D, Miodragovic Z, Andelkovic K,Miodragovic D. Eur. J. Med.Chem. 44 2009 1537-1544. | 19.Geary W.J., Coord. Chem. Rev, 1971, 7, 81. | 20. John R.P., Sreekanth A., Kurup M.R.P,. Usman A,. Razak I.A. Fun H.- K.Spectrochim. Acta A 59 2003 1349. | 21. Nazimuddin M. Ali M.A., Smith F.E., Polyhedron 10 1991 327. | 22. Bermejo E. Carballo R., Castineiras A., Dominguez R. Liberta A. E., Maichle-Mossmer C., West D. X. , Naturforsch Z. B: Chem. Sci. 54 1999 777. | 23.. Castineiras A,. Bermejo E, West D. X., Ackerman L.J., Martinez J. V,.Ortega S. H. Polyhedron 18 1999 1469. | 24. Naik A.D., Revankar V.K., Proc. Indian Acad. Sci (Chem. Sci.) 113 2001 285. | 25. Philip V., Suni V.,Kurup M.R.P Polyhedron 25 2006 1931. | 26.. Li I.X., Tang H.A., Yi-Zhi Li.,Wang M., Wang L.F., Xia C.G.J. Inorg.Biochem. 78 2000 167. | 27. John R.P., Sreekanth A., Rajakannan V., Ajith T.A., Kurup M.R.P.,Polyhedron 23 2004 2549. | 28. Nakamoto K., Infrared and Raman Spectra of Inorganic and Coordination compounds, 5"' ed., Wiley, New York, 1997. | 29. Bindu P. Kurup M.R.P., Satyakeerthy T.R. Polyhedron 1.8 1999 321. | 30. West D.X.,Whyte A.C Sharif F.D.,Gabremedhin H., Liberta A.E. Trans.Met. Chem. 18 1993 238. | 31.Inskeep R.G., J. Inorg Nucl-Chem, 24 1962 763. | 32.Schilt A.A., Taylor R.C., J. Inorg. Nucl. Chem. 9 1959 217. | 33.Monoyama M., Inorganic Chim Acta, 13 1975 5. | 34.Mohamed G.G., Nour-El Dien FA, El-Gamel E.A., J. Therm. Anal. Cal, 67 2002 135. | 35.Shrivastava R.S., Inorg. Chimica Acta, 1981, Vol 56, 65. | 36.Mitic D,Milenkovic M. Milosavljevic S, Godevac D, Miodragovic Z, Andelkovic K,Miodragovic D. 44, 2009 1537.