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Metal Complexes of Acetone Thiosemicarbazone: Synthesis, Spectral Characterization and Pharmacological Studies

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Abstract: Acetone thiosemicarbazone (ACTSC) a very versatile Schiff base ligand reacted with some transition metals forming co-ordination complexes. These solid complexes have been isolated and characterized on the basis of elemental analysis and spectroscopic studies (UV-Vis, FT-IR and ^{1}H-NMR). The infrared spectra of the complexes revealed bands at (736-864 nm) and (1608-1627 nm) attributed to (>C=S*)* and (>C=N) respectively. These bands experienced a negative shift when compared to the spectral of the parent ligand. The electronic absorption spectra of the ligand shows a band around (198-200 nm) corresponding to the NH-C=S group, also a band due to the C=N chromophore in the spectrum of ligand at 294 nm (π-π^* transition) undergo bathochromic shift to (310-336 nm) in the spectra of metal complexes. The ligand and the corresponding metal complexes were screened for their antifungal activities against *Aspergillus niger*, *Penicillium species*, *Rhizopus* and *Candida albicans* using adapted qualitative diffusimetric method. The most active complex is $Cu(ACNT)_2Cl_2$ with (27.67±0.58 mm) against *Rhizopus.* The activities of the metal complexes were found to be greater than that of the ligand. Toxicity effects of administration 50 mg/kg body weight of the control group showed that AST(20.67 ± 1.53 µ/L), ALT(22.33 ±2.08 µ/L), and ALP(30.67 ± 2.08 µ/L) which are quite significantly different ($P<$ 0.05) from that of ACTSC which gave AST(25.67 ± 2.52 µ/L), ALT(27.67 ± 1.53 µ/L) and ALP(54.00 ± 3.05 µ/L) an indication of liver derangement. 25 and 50 mg/kg body weight of $Ni(ACNT)_2SO_4$, $Zn(ACNT)_2Cl_2$, $Cu(ACNT)_2Cl_2$ and $Cu(ACNT)_2SO_4EtOH$ on the liver enzyme showed no significant difference ($P\geq 0.05$) when compared to the control group which is an indication of little or no toxicity. The study however showed that complexation of the ligand with metal ion increases the activity of the complexes and also reduces their toxicity level.
Keywords: Acetone thiosemicarbazone, spectral, antifungal activity, liver enzyme.

1 Introduction

Thiosemicarbazones are compounds of considerable interest because of their important chemical properties and potentially beneficial biological activities [1-3]. They display a broad spectrum of pharmacological properties, including antitumor, antifungal, antibacterial, antiviral and antimalarial activities [4]. Thiosemicarbazones derived from the combination of thiosemicarbazide with an aldehyde or ketone are very versatile Schiff base ligands that show a variety of coordination modes in metal complexes [5-7].

They can act as a monodentate ligand that binds to the metal ion through the thioketo sulphur atom or as a bidentate ligand that coordinates to the metal ion through the sulphur atom and one of the nitrogen atoms of the hydrazine moiety to form four or five membered chelate rings [5-8].

2 Material and Methods

All chemicals used were of A.R. grade. The ligand and complexes were synthesized using standard procedure. The metal salts used are $CuSO_4.5H_2O$, $NiSO_4.6H_2O$, $ZnCl_2$ and $CuCl_2.2H_2O$. Melting points of complexes were determined using electrically heated Griffin melting point apparatus. The conductivity measurements were taken using Jenway 4510 Conductivity Meter. The CHN Elemental Analysis was done using Thermo Flash 1112 CHNSO Elemental Analyser. Electronic spectra of the ligand and the complexes were recorded in Dimethylsuphoxide (DMSO) solution on Shimadzu 10UV scanning Uv-Visible spectrophotometer in the range 200 – 800 nm. The infrared (IR) spectra were recorded on Shimadzu 8400S FTIR spectrophotometer as KBr pellets in the range 4000 – 400 cm^{-1}. All the synthesized compounds were screened for their antifungal activities using sensitivity disc method.

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3 Experimental

3.1 Synthesis of Acetone Thiosemicarbazone (ACTSC)

Thiosemicarbazide (0.01 mol 0.182 g) was dissolved in methanol (30 mL) by refluxing at 50 °C. In the refluxing solution; acetone 0.1 mol (0.87 mL) solution in methanol (30 mL) was added, this was then followed by the addition of few drops of concentrated HCl. The reaction mixture was continuously stirred and refluxed for 4 h at 60 °C. The volume of reaction mixture was reduced and then cooled on ice water. The crystals of acetone thiosemicarbazone precipitated out, it was washed with methanol and dried in the desicator over silica gel [9-12].

3.2 Synthesis of Metal Complexes of Acetone Thiosemicarbazone

The metal complexes of ACTSC were prepared by a slow addition of 1 mmol of the metal salt solution in 15 mL methanol to (2 mmol, 0.234 g) hot stirring methanolic solution (30 mL) of ACTSC in the molar ratio of 2:1. The reacting mixture was continuously stirred and refluxed for 2-3 h. The product formed was collected by filtration, washed with cold methanol, and dried in the desiccator over silica gel [10, 13].

3.3 Antifungi activity

The antifungi activities of ACTCS and its complexes were screened by adapted qualitative diffusimetric method. Plates were filed with the SDA agar (two-thirds), the fungi specie inoculated into it and the sample solutions added and incubated at 37 ^{o}C for 72 hours.

3.4 Biochemical Assay

The following liver function test were carried out to determine the derangement in the liver of the animals used for the study; alanine aminotransferase (ALT), aspartate aminotransferase (AST), were determined by the colorimetric method of Reitman and Frankel, 1957 using a commercial assay kits from Randox laboratories Ltd Co. Antrim, United Kingdom. While and alkaline phosphatase (ALP) by the colorimetric method of REC, 1972 using assay kits from Randox laboratories Ltd.

4 Results and Disscusion

4.1 Physical Characteristics of ACTSC and its Metal Complexes

Physical characteristics, molecular weight, melting point and conductivity data of ACTSC and its metal complexes are presented in Table 1. The colour exhibited by the metal complexes in may be due to d-d electron transition or as a

Table 1: Physical Characteristics and Micro-analytical data of ACTSC and its Metal Complexes.

					Elemental Analysis Found/ (Calcd) (%)			
Formulation and Empirical Formula	**M/ Wt. (g/mol)**	**Colour**	**Yield (%)**	**M.p. (^{o}C)**	**C**	**H**	**N**	**EC 10^{-3} M (ohm^{-1} cm^{2} mol^{-1})**
ACTSC $C_4H_9N_3S$	131	White crystals	89	181.9	36.51 (36.62)	6.89 (6.91)	32.25 (32.03)	
$Ni(ACTSC)_2SO_4$ $C_8H_{18}N_6NiO_4S_3$	417	Brown powder	69	355 (DT)	23.34 (23.04)	4.97 (4.35)	20.98 (20.15)	13.14
$Zn(ACTSC)_2Cl_2$ $C_8H_{18}C_{l2}N_6S_2Zn$	399	White crystals	49	290	24.54 (24.10)	4.96 (4.55)	21.44 (21.08)	12.10
$Cu(ACTSC)_2SO_4EtoH$ $C_{10}H_{24}CuN_6O_5S_3$	468	Black powder	65	183.5	26.01 (25.66)	5.86 (5.17)	17.98 (17.95)	20.12
$Cu(ACTSC)_2Cl_2$ $C_8H_{18}Cl_2CuN_6S_2$	397	Green powder	62	231	24.68 (24.21)	4.86 (4.57)	21.38 (21.18)	18.12

result of electron transfer (lone pair) from the ligand to the central metal [14].The increase in melting point of the complexes observed when compared with the ligand could be attributed to the increase in molecular mass of the resulting complexes [15]. The molar conductance values of the complexes in DMSO fall in the range 12 - 21 $\Omega^{-1}cm^2$ mol^{-1} indicating that the complexes are non-electrolyte.

4.2 Electronic Spectra nm (cm^{-1}) of ACNT and its Metal Complexes

ACTSC in Table 2 showed absorption bands in the region 207 nm (48309), 215 nm (46511), 236 nm (42372) and 304 nm (32894) cm^{-1} corresponding to $\pi \rightarrow \pi^*$ [16]. A blue shift was observed upon complexation caused by the polarization in the C=N bond due to metal ligand electron interaction during the chelation. This also indicates the coordination of azomethine nitrogen to the metal atom.

In octahedral Ni(II) complexes, three spin-allowed transitions are expected because of the free-ion ground ^3F term and the presence of ^3P term. The d-d transitions: $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{lg}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{lg}(P)$ generally occurred within the ranges 7000-13000, 11000-20000 and 19000-27000 cm-^{1} respectively. The electronic spectrum of the $Ni(ACTSC)_2$ complex shows five bands: 200(50000), 214(46728), 230(43478), 251(39840) and 293(34129) assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. $Ni(ACTSC)_2$ did not show band corresponding to LMCT and d-d transition, these transitions may have been submerged by other more intense transition because of their low intensity as reported by other workers [17-18]. It can thus be inferred that the $Ni(ACTSC)_2$ complex has a square planar geometry.

In the octahedral Cu(II) complexes, a band in the visible spectrum corresponding to the $^2E_g \rightarrow T_{2g}$ transition is expected, but due to strong Jahn-Teller distortion, octahedral Cu(II) complexes often give broad bands resulting from several overlapping bands or, where the bands are resolved up to three close bands [19]. The electronic spectrum of $Cu(ACTSC)_2SO_4$ shows a broad asymmetric band at ca. 446(22421). This confirms the octahedral stereochemistry proposed for the complex. The spectrum also shows absorption bands at 200, 208, 218 and 310 nm. These three bands are due to the ligand absorption, which were shifted from that of the parent ligand upon complex formation.

Table 2: Electronic Spectra nm (cm^{-1}) of ACTSC and its Metal Complexes.

Compound	Electronic Configuration	n →π*	π →π*	Charge Transfer	d–d
ACTSC	-	207 (48309) 215 (46511) 236 (42372)	304 (32894)	-	-
$Ni(ACTSC)_2SO_4$	d^8	200 (50000) 214 (46728) 230 (43478) 251 (39840)	293 (34129)	-	-
$Zn(ACTSC)_2Cl_2$	d^{10}	200 (50000) 208 (48076) 224 (44642) 229 (43668)	316 (31645)	-	-
$Cu(ACTSC)_2SO_4$ EtoH	d^9	200 (50000) 208 (48076) 214 (46728) 218 (35714)	310 (32258)	-	446 (22421) $^2B_{1g} \rightarrow {}^2E_g$
$Cu(ACTSC)_2Cl_2$	d^9	201 (49751) 221 (45248) 240 (41666)	261 (38314) 276 (36231)	362 (27624)	-

4.3 IR Spectra of ACTSC and its Metal

Complexes

Table 3: The Main IR (cm^{-1}) of ACTSC and its Metal Complexes

IR Band Assignment (KBr, cm^{-1})	ACTSC	$Ni(ACTSC)_2SO_4$	$Zn(ACTSC)_2Cl_2$	$Cu(ACTSC)_2SO_4EtOH$	$Cu(ACTSC)_2Cl_2$
ν(OH),H_2O				3481 br 3416 br	
ν(N-H)	3377 s 3230 s 3155 s	3298 m	3294 br 3182 br	3286 br 3163 br	3419 br 3047 br
ν(C=N)	1658 s	1616 s	1608 s	1627 s	1627 s
n(C-S)+n(C-N)	1269 s	1265 m	1274 s	1267 s	1205 s
ν(N-N)	1028 s	1072 w	1116 s	1074 w	1043 s
ν(C=S)	866 s 788 s	864 w 717 m	736 m	854 w 719 s	844 m 781
M-N		430 w	471 w	448 w	461 w
M-S		414 w	449 w	447 w	430 w

KEY: ***s = strong, w = weak, m = medium, br. = broad***

The infrared spectra of ACTSC ligand Table 3 showed a strong band at 1645 cm^{-1} attributed to C=N group [20-21]. A negative shift of the order 31-42 cm^{-1} was observed for C=N stretching vibration on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation which is in agreement with the work reported by [21-22]. The next strong band at 866-788 cm^{-1} is attributed to C=S group, a negative shift in the region of 864-717 and 854-719 cm^{-1} was observed in the complexes on coordination thereby indicating the involvement of thio sulfur in the coordination the metal ion [21, 22, 6]. The bands in the range 3481-3416 and 3377-3047 cm^{-1} are attributed to ν(OH, H_2O) and ν(NH, NH_2). The negligible effect on these frequencies after complexation precludes the possibility of complexation at this group. $Cu(ACTSC)_2SO_4$ complex showed bands at 613-616 and 1117-1140 cm^{-1} which were attributed to the presence of ionic sulfate [23]. On the other hand, the spectra of the complexes showed new bands around 530-530, 430-448 and 414-447 cm^{-1} due to νM-O, νM-N and νM-S respectively [21-23]. The presence of these bands supported the formation of the complexes.

4.4 ^1H NMR Spectra of ACTSC and its Metal Complexes

The ^1H -NMR spectral data (δ, ppm) recorded in DMSO-d_6 of ACTSC, $Cu(ACTSC)_2Cl_2$ and $Cu(ACTSC)_2SO_4$ EtOH only are presented in Table 4 . The spectra showed no peak at 4 ppm, that is attributable to SH protons [24]. A peak at 7.68-7.99 ppm, attributed to the N–H group, indicating that the ligand was in the thione form, which is in conformity with the IR spectrum. The methyl signals from the coordinated thiosemicarbazone in the complexes were observed at 1.95-2.49 ppm. A significant azomethine proton signal due to CH=N was observed at 7.00-9.90 ppm. The downfield shifts of the N-H and N_2H signals are attributable to coordination through the azomethine nitrogen atom and the thiocarbonyl sulfur atom, which are in consistent with the IR spectral data. These observations are in agreement with the findings of previous workers [25-26].

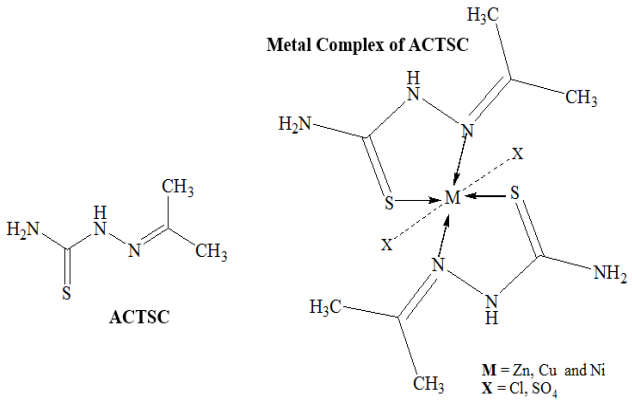

Fig. 1: Proposed structures of ACTSC and its Complexes

Table 4: ^{1}H NMR Spectra data (δ, ppm) of ACTSC and its Metal Complexes

Compound	-CH_3 (Methyl Proton)	-$^{4}NH_2$ (Imino Proton)	-^{2}NH (Azometine Proton)	-OH (Alcohol)	Chemical Formula
ACTSC	6H, 1,3 (s), 1.91 1.92	2H, 8(s), 7.51, 7.99	1H, 5(s), 9.90		$C_4H_9N_3S$
$Cu(ACTSC)_2Cl_2$	12H, 3,4(s), 1.98 1.20 2.29-2.29	4H, 2 2,(s), 6.71 2H,5 (d), 3.90	1H, 4(s), 7.00		$C_8H_{18}Cl_2CuN_6S_2$
$Cu(ACTSC)_2SO_4$ EtOH	12H 7,8 (s), 2.49	2H, .2,2 (s), 7.76 2H,(d), 3.56	2H, 4, 4 (s), 9.15- 10.94	6H, 1 (m) 2.80	$C_{10}H_{24}CuN_6O_5S_3$

4.5 Antifungal Activities of ACTSC and its Complexes

The quantitative anti-microbial activity test results as presented in Tables 5 proved that both the ligand and the complex combinations have specific activity, depending on the pathogenic microbial species tested. The metal chelates are more potent than the chelating agent (free ligand). This enhancement in the activity of the metal complexes can be explained on the basis of chelation theory. It is however known that chelating tends to make the Schiff base act as more powerful and potent bactereostatic agent, thus inhibiting the growth of bacteria and fungi [27-28]. Chelation induced significant changes in the biological activity of the ligand. A possible explanation for the observed increased activity upon chelation is that the positive charge of the metal in chelated complex is partially shared with the ligand's donor atoms so that there is **π**-electron delocalization over the whole chelate ring [29]. Subsequently, this reduces the polarity of the metal ion and which in turn will increase the lipophilic character of the metal chelate and favors its permeation through the lipoid layers of the bacterial membranes [30].

Table 5: Antifungal Activities of ACTSC and its Complexes

Test Samples	*Aspergillus niger*	*Penicillium Species*	*Rhizopus*	*Candida albicans*
ACTSC	$11.33 \pm 1.47^{**}$	$10.23 \pm 0.58^{**}$	$10.00 \pm 2.00^{**}$	$9.00 \pm 1.00^{**}$
$Ni(ACTSC)_2SO_4$	$22.00 \pm 2.00^{**}$	$20.00 \pm 0.00^{**}$	$21.00 \pm 1.73^{**}$	$19.67 \pm 2.08^{**}$
$Zn(ACTSC)_2Cl_2$	$19.67 \pm 1.53^{**}$	$16.00 \pm 1.00^{**}$	$11.33 \pm 1.15^{**}$	$0.33 \pm 0.58^{*}$
$Cu(ACTSC)_2SO_4EtoH$	$22.33 \pm 2.08^{**}$	$21.00 \pm 2.00^{**}$	$23.66 \pm 2.52^{**}$	$23.00 \pm 1.00^{**}$

4.6 Toxicity Effects of Complex of ACTSC and its Metal Complexes on Liver Enzymes.

Toxicity effects of administration 50 mg/kg body weight of the control group as presented in Table 6 showed that AST(20.67±1.53 µ/L), ALT(22.33±2.08 µ/L), and ALP(30.67±2.08 µ/L) are quite significantly different (P<0.05) from that of ACTSC which gave AST(25.67±2.52 µ/L), ALT(27.67±1.53 µ/L) and ALP(54.00±3.05 µ/L) an indication of liver derangement. Meanwhile, 25 and 50 mg/kg body weight of $Ni(ACTSC)_2SO_4$, $Zn(ACTSC)_2Cl_2$, $Cu(ACTSC)_2Cl_2$ and $Cu(ACTSC)_2SO_4EtOH$ on the liver enzyme showed no significant difference (P≥0.05) when compared to the control group which is an indication of little or no toxicity [31].

Table 6: Toxicity Effects of ACTSC and its Metal Complexes on Liver Enzymes of Wistar rats.

Groups	Aspartate Aminotransferase (AST µ/L)	Alanine Transferase (ALT µ/L)	Alkaline Phospatase (ALP µ/L)
CONTROL 5% DMSO	20.67 ± 1.53^{a}	22.33 ± 2.08^{a}	30.67 ± 2.08^{a}
25 mg/kg ACTSC	24.00 ± 1.73^{b}	26.00 ± 1.00^{b}	48.00 ± 3.00^{b}
50 mg/kg ACTSC	25.67 ± 2.52^{c}	27.67 ± 1.53^{c}	54.00 ± 3.05^{c}
25 mg/kg $Zn(ACTSC)_2Cl_2$	21.33 ± 1.53^{a}	23.00 ± 2.00^{a}	32.60 ± 2.08^{a}
50 mg/kg $Zn(ACTSC)_2Cl_2$	24.00 ± 1.00^{d}	24.66 ± 1.53^{a}	36.70 ± 2.52^{d}
25 mg/kg $Cu(ACTSC)_2SO_4EtoH$	21.00 ± 2.00^{a}	22.30 ± 2.05^{a}	32.70 ± 2.50^{a}
50 mg/kg $Cu(ACTSC)_2SO_4EtoH$	21.67 ± 2.08^{a}	23.60 ± 1.52^{e}	33.00 ± 2.00^{a}
25 mg/kg $Ni(ACTSC)_2SO_4$	20.33 ± 2.52^{a}	23.70 ± 2.50^{a}	31.00 ± 2.65^{a}
50 mg/kg $Ni(ACTSC)_2SO_4$	21.33 ± 1.53^{a}	25.00 ± 2.00^{a}	33.00 ± 3.00^{a}

Values are mean of triplicate determinations ± standard deviation, values in the same column with different superscript letters are significantly different from the control (P< 0.05), one way analysis of variance (ANOVA) followed by post hoc LSD.

5 Conclusion

The ligand, acetone thiosemicarbazone and its metal complexes were synthesized and characterized. It is examined that in these complexes the ligand has NS donor bidentate nature. The biological behavior revealed that free thiosemicarbazone has poor antifungi activity against selected test fungi, the Zn complex showed moderate activity, while complexes of Ni and Cu have effective antifungi activity. The chelation induced significant changes in the biological activity of the ligand.

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References

[1] M. J. M. Campbell; *Coordination Chemistry Review*, **(1975)**, 15: 279-319.

[2] S. Padhye, G. B. Kanflman; *Coordination Chemistry Review*, **(1985)**, 63: 127.

[3] D. X. West, A. E. Liberta, K. G. Rajendran, I. H. Hall; *Anti-cancer Drugs*, **(1997)**, 4**:** 241-249**.**

[4] H. Beraldo, D. Gambino; *Mini-Review of Medicinal Chemistry* **(2004)**, 4: 31-39.

[5] W. Kaminsky, J. P. Jasinski, R. Noudenberg, K. I. Goldberg, D. X. West; *Journal of Molecular Structures*, **(2002)**, 23 135-141**.**

[6] M. Baldini, M. B. Ferrari, F. Bisceglie, G. Pelosi, S. Pinelli, P. Tarasconi; *Inorganic Chemistry*, **(2003)**, 42(6): 2049-2055.

[7] A. P. Rebolledo, M. Vieites, D. Gambino, O. E. Pir,o, E. E. Castellano, C. L. Zani, E. S. Fagundes, L. R. S. Teixeira, A. A. Batista, H. Beraldo; *Journal of Inorganic Biochemstry*, **(2005)**, 99: 698-706.

[8] S. Chandra, P. Ballabh, S. K. Choudhary; *International Journal of Applied Biology and Pharmaceutical Technology*, **(2013)**, 4(3): 64-72.

[9] T. S. Lobana, A. S´anchez, J. S. Casas; *Journal of the Chemical Society*, **(1997)**, 22: 4289–4300.

[10] Y. K. Gupta, S. C. Agarwal, S. P. Madnawat, N. Ram; *.International Journal of Research in Chemistry and Environment*, **(2012)**, 2(2).

[11] S. Sugam, D. G. Mangla; *Journal of Chemical Pharmacology Research*, **(2011)**, 3(6):1009-1016, 1009.

[12] B. C. Mahto; *Journal of Indian Chemical Society*, **(1981)**, 8: 935-938.

[13] S. Kumar, Y. Kumar; *International Current Pharmaceutical Journal*, **(2013)**, 2(4): 88-91.

[14] M. A. Oladipo, J. A. O. Woods, O. A. Odunola; *Science Focus*, **(2005)**, 10(1): 49-52.

[15] H. A. Zeinab; *New Journal of Chemistry*, **(2006)**, 10(38):1016-1017.

[16] F. A. Cotton, G. Wilkinson, Basic *Inorganic Chemistry*. Wiley Eastern Limited. Canada. **(1986)**

[17] J. A., Obaleye, C. L. Orjiekwe, D. A. Edwards; *Bulletin of Chemical Society of Ethiopia*, **(1999)**, 13(1): 1.

[18] F. H. Merguarant; Journal *Chemical. Society*, **(1966)**, B. 1242

[19] A. B. P. Lever; *Journal of Chemical Education*, **(1968)**, 45:711-712.

[20] Z. H. Abd El-Wahab, M. M. Mashaly, A. A. Salman, B. A. El-Shetary, A. A. Faheim; *Spectrochimica Acta, Part A*., **(2004)**, 60(12): 2861–2873.

[21] E. Bermejo, A. Castineiras, I. Garcia-Santos, D. X. West; *Journal of Inorganic Chemistry* **(2005)**, 63(1): 2011-2019.

[22] M. C. Aguirre, J. Borras, A. Castineiras, J. M. Gurcia-Monteagudo, I. Garcia-Santos, J. Niclos, D. X. West; *European Journal Inorganic Chemistry*, **(2006)**, 10: 1231-1244.

[23] K. Nakamoto; *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley-Interscience, New York. 86. **(1997).**

[24] E. M. Jouad, G. Larcher, M. Allain, A. Riou, G. M. Bouet, A. M. Khan, X. D. Thanh; *Journal Inorganic Biochemistry*, **(2001)**, 86: 565.

[25] H. Sarmistha, P. Shie-Ming, L. Gene-Hsiang, C. Tanmay, M. Asama, D. Sushanta, S. Utpal, B. Samaresh; *New Journal of Chemistry*, **(2007)**, 23(67): 256-269**.**

[26] R. Gangadharan, S. Chirakuzhi, R. Amritha, A. John, T. C. Vino; *Journal of the Serbian Chemical Society*, **(2010)**, 75(6): 749–761.

[27] M. A. Salam, M. A., Affan, S. Ramkrishna, B. A. Fasihuddin, S. Norrihan;*Bioinorganic Chemistry and Applications*, **(2012)**, Article ID 698491: 9

[28] R. S. Sarivactava; *Inorganic Chimica Acta*, **(1981)**, 55: 71-74.

[29] N. Fahmi, I. J. Gupta, R. V. Singh; *Phosphours Sulfur and Silicon*. **(1998)**, 132:1.

[30] S. K. Sengupta, O. P. Pandey, B. K. Srivastava, V. K. Sharma; *Transition Metal Chemistry*, **(1998)**, 23(4): 49–353.

[31] E. D. Kpomah, E. M. Arhoghro, A. A. Uwakwe; *Journal of Natural Sciences Research*, **(2012)**, 2(6): 22-28.