International Journal of Engineering, Science and Mathematics
Vol. 7 Issue 11, November 2018,
ISSN: 2320-0294 Impact Factor: 6.765
Journal Homepage: http://www.ijesm.co.in, Email: ijesmj@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

ANTIMICROBIAL ACTIVITIES AND SPECTROSCOPIC STUDIES OF Co(II) AND Zn(II) MIXED LIGAND COMPLEXES DERIVED FROM ISONICOTINYLHYDRAZIDE AND VANILLIN WITH NITROGEN, SULPHUR AND OXYGEN MONODENDATE LIGANDS

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Abstract
The ligand, isonicotinylhydrazone-4-hydroxy-3-methoxybenzaldehyde (ISVN) was synthesized by the condensation reaction between isonicotinylhydrazide and 4-hydroxy-3-methoxybenzaldehyde **(**vanillin) at room temperature. The synthesized ligand was used to prepare the mixed ligand complexes of Co(II) and Zn(II) with aniline, furan and thiophene as secondary ligands. These complexes were characterized by using conductometry, elemental analysis, infrared and UV spectroscopic analysis. The melting points of the synthesized compounds were high (221.4 - 238.4 ^{o}C) while the conductivities were low (0.09 - 1.19 µs). The infrared spectral data available proved that the ligand, ISVN coordinated to the metal ions through its nitrogen atom of the azomethine group and the phenolic oxygen atom of the vanillin ring thus illustrating the bidentate nature. The secondary ligands; aniline, furan and thiophene coordinated to the metal ions through their donor atoms *viz* nitrogen, oxygen and sulphur respectively. The electronic absorption bands depicted $^{4}T_{Ig} \rightarrow {}^{4}A_{2g}$ and $^{4}T_{Ig} \rightarrow {}^{4}{}_{T2g}$ transitions for the Co(II) complexes revealing an octahedral geometry for the molecule while Zn(II) ion with no d-d transition show a band indicating charge transfer at 24,330cm^{-1} which is typical of tetrahedral geometry. The antimicrobial analysis was carried out using disc diffusion method on strains of *Escherichia coli, Staphylococcus aureus and Salmonella typhi—the bacteria.* The zones of inhibition (24.0-38.0mm and 23.0-34.0 mm)) caused by the cobalt and zinc complexes were significantly higher than that caused by streptomycin (24.0-26.0 mm) while the zones of inhibition on fungi i.e *Candida albican, Trichophyton rubrum and Aspergillus niger* caused by the same complexes were comparable with those caused by fluconazole. The minimum inhibitory concentrations (MICs) obtained for the ligand and the complexes were in the range of 2.5-10 mg/ml. The analysis proved that the synthesized compounds were bactericidal and fungicidal within the range of 2.5- 10 mg/ml
Key words: synthesis, characterization, antimicrobial, ligand, complex.

Introduction
Schiff bases are compounds containing the -C=N- azomethine functional group.[1]. They are also called imine and are readily prepared by the condensation reaction between an aldehyde or ketone and amine [2,3]. The reaction precedes best at pH of 4 and 5. Schiff bases as Lewis bases are ligands, electrons donors, easily coordinate to transition metal ions to form complexes [4]. The methods of preparation and their versatile mode of coordination have made their study gain a lot of significant importance [5]. Schiff bases have been applied in many fields of human endeavors which include medicine, food industries, chemical industries, agriculture, and analytical studies [6]. Due to the chelating nature of the azomethine group, Schiff bases and their complexes are used as antibacterial,

antifungal, anti-inflammatory, insecticides, herbicides [2,7,11], antitumor and [8,9], DNA binding and cleaving agents [10] and anticancer agents [12]. In inorganic chemistry, Schiff bases and their complexes have been used as catalysts for many reactions such as oxidation, reduction and polymerization reactions [13]. Their roles as catalyst in many enzymatic reactions have also been reported [14]. Schiff bases are used as liquid crystals, and also in the preparation of a-aminophosphonate ester and H-phosphonate ester with repeatable

Pudovik reaction which possess bioactivity such as inhibitor to cancer and viruses and as antibiotic [15]. In view of the numerous applications and the fact that complexes of this class are structure- activity related, hence potency can be enhanced by configurational modifications, the present focused on synthesis, characterization and antimicrobial studies.

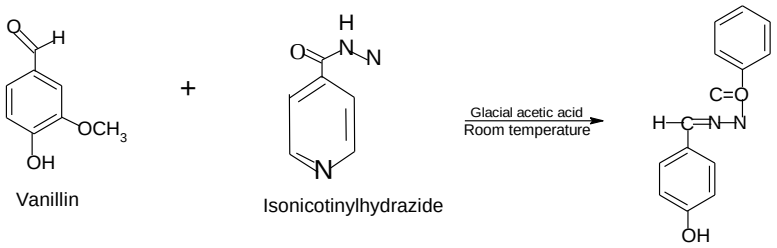
Experimental

All chemicals used for this research were of analytical grade purchased from Sigma Aldrich and were used without further purification. Shimadzu FTIR-8400S,Shimadzu UVD2960 spectrophotometer for electronic absorption, Gallenkemp melting point apparatus, Perkin Elmer elemental analyzer, Jenway 4510 conductivity bridge with conventional dip-type black electrode for conductance, Uniscope SM 9053 Laboratory oven, nutrient agar, potato dextrose agar, and autoclave.

Synthesis of the ligand

Isonicotinylhydrazide (1.371g, 0.01mol) in 20ml ethanol was mixed with vanillin (0.01 mol, 1.521 g) and stirred vigorously for 2 minutes using a magnetic stirrer. Five drops of glacial acetic acid was added as stirring continued for 2 hours. The solution was allowed to stand undisturbed over night. The white precipitate formed was filtered, washed with ethanol, recrystallized with hot methanol and dried over fused calcium chloride in a desiccator [11,16, 17].. The percentage yield was calculated.

The equation for the reaction is:



Synthesis of Co(II) or Zn(II) mixed ligand complexes

A solution of metal (II) chloride (0.01mol) in 50ml ethanol was added to the synthesized isonicotinylhydrazone-4-hydroxy-3-methoxybenzaldehyde (0.01mol) and stirred for 15 minutes, 20ml of aniline, furan or thiophene was added and stirred for 2 hours. The precipitate formed was filtered, washed with ethanol, recrystallized with hot methanol and dried over fused calcium chloride in a desiccator [11,17].

Results and discussion

Table 1: Physical data of the ligands and the complexes

Compounds	Colour	Melting point (^{0}C)	Conductivity (µs)	Yield %	Found/ Calcd % M	C	H	N	S
ISVN	Pale yellow	237.5	0.11	71.82	-	62.2 (62.0)	4.4 (3.9)	15.6 (15.2)	
$[Co(ISVN)_2(A)_2]$ $CoC_{38}H_{30}N_8O_6$	Yellow	238.4	0.60	51.48	7.8 (7.7)	60.6 (59.8)	4.0 (3.9)	14.9 (14.6)	-
$[Co(ISVN)_2(F)_2]$ $CoC_{36}H_{32}N_6O_8$	Yellow	221.4	1.05	57.4	8.0 (8.2)	58.8 (60.2)	4.4 (4,2)	11.8 (11.6)	-
$[Co(ISVN)_2(T)_2]$ $CoC_{36}H_{32}N_6O_6S_2$	Yellow	281.9	0.09	56.47	7.7 (7.7)	56.3 (64.3)	4.3 (4.3)	11.0 (13)	8.3 (8.20)
$[Zn(ISVN)_2(A)_2]$ $ZnC_{38}H_{30}N_8O_6$	Pale yellow	235.4	1.04	51.48	8.6 (8,5)	60.6 (60.5)	3.9 (3.8)	14.8 (14.3)	
$[Zn(ISVN)_2(F)_2]$ $ZnC_{36}H_{32}N_6O_8$	Pale yellow	229.7	0.19	49.85	8.8 (8.7)	58.3 (58.4)	4.3 (4.6)	11.3 (10.9)	-
$[Zn(ISVN)_2(T)_2]$ $ZnC_{36}H_{32}N_6O_6S_2$	Pale yellow	236.8	1.91	49.58	8.4 (8.3)	55.9 (55.6)	4.1 (5)	10. 8 (11.2)	8.3 (8.0)

Table 3: Infrared spectra of the ligand and the complexes

Compounds	v(O-H)	v(N-H)	v(C=O)	v(C=N)	v(M-N)	v(M-O)	v(M-S)
ISVN	3466	2923	1664	1594			
$[Co(ISVN)_2(A)_2]$	3342	2923	1664	1552	601	413	
$[Co(ISVN)_2(F)_2]$	3324	2923	1664	1552	600	403	
$[Co(ISVN)_2(T)_2]$	3376	2923	1663	1551	620	418	401
$[Zn(ISVN)_2(A)_2]$	3296	2923	1660	1550	590	411	
$[Zn(ISVN)_2(F)_2]$	3507	2923	1664	1548	471	435	
$[Zn(ISVN)_2(T)_2]$	3510	2923	1664	1549	722	416	400

Table 5: Zones of inhibition

Compounds	*S. typhi*	*E. coli*	*S. aureus*	*A. niger*	*T. rubrum*	*C. albicans*
ISVN	14.0	16	17	11	12	12
$[Co(ISVN)_2(A)_2]$	32.0	34	38	20	24	31
$[Co(ISVN)_2(F)_2]$	25.0	24	26	20	19	20
$[Co(ISVN_2(T)_2]$	27.0	33	35	23	26	28
$[Zn(ISVN)_2(A)_2]$	26.0	24	34	28	22	21
$[Zn(ISVN)_2(F)_2]$	23.0	24	31	23	22	23
$[Zn(ISVN)_2(T)_2]$	31.0	34	33	24	22	26
Streptomycin/fluconazole	24	26	25	23	23	22

Table 6: Minimum inhibitory concentration

Compounds	*S. typhi*	*E. coli*	*S. aureus*	*A. niger*	*T. rubrum*	*C. albicans*
ISVN	10.0	5.0	5.0	10.0	5.0	5.0
$[Co(ISVN)_2(A)_2]$	2.5	2.5	2.5	2.5	2.5	10.0
$[Co(ISVN)_2(F)_2]$	2.5	2.5	2.5	5.0	2.5	5.0
$[Co(ISVN)_2(T)_2]$	2.5	2.5	5.0	5.0	5.0	2.5
$[Zn(ISVN)_2(A)_2]$	2.5	2.5	2.5	2.5	2.5	2.5
$[Zn(ISVN)_2(F)_2]$	5.0	2.5	2.5	5.0	2.5	5.0
$[Zn(ISVN)_2(T)_2]$	2.5	2.5	2.5	5.0	5.0	2.5

Table 7: Minimum bactericidal concentration

Compounds	*S. typhi*	*E. coli*	*S. aureus*	*A. niger*	*T. rubrum*	*C. albicans*
ISVN	10.0	5.0	2.5	10.0	10.0	10.0
$[Co(ISVN)_2(A)_2]$	2.5	2.5	2.5	10.0	5.0	10.0
$[Co(ISVN)_2(F)_2]$	2.5	2.5	2.5	10.0	2.5	10.0
$[Co(ISVN)_2(T)_2]$	2.5	2.5	5.0	5.0	10.0	5.0
$[Zn(ISVN)_2(A)_2]$	5.0	2.5	2.5	5.0	5.0	5.0
$[Zn(ISVN)_2(F)_2]$	10.0	2.5	2.5	10.0	5.0	10.0
$[Zn(ISVN)_2(T)_2]$	5.0	2.5	2.5	10.0	5.0	5.0

Discussion

The physical properties of the synthesized compounds are recorded in Table 1. They include colour, melting points, physical nature and molar conductivity measurement. All the complexes were thermally stable, variedly coloured and insoluble in organic solvent but readily soluble in coordinating solvents like DMF, DMSO etc. The ligand and the mixed ligand complexes were powdery in nature, melted at sharp and high temperatures ranging from 221.4 to 281.8^{oC}. These tend to indicate the strong bonding network of the polymeric system. The sharpness in melting had to do with the level of purity and they all melted with decomposition which was indicated by change in colour. The conductivities values were rather very low revealing the non electrolytic nature of the chelates. The elemental analysis affirmed the purity state of the complexes and the ratio of metal to ligand.

Infrared Spectra

The infrared spectral data of the ligand and its complexes are presented in Table 2. From the IR spectra of the ligand, the vibrational frequencies at 1594 cm^{-1} was assigned to the υ(C=N) stretching. This band exhibited a systematic shift to higher frequencies of 1552-1548 cm^{-1} in the spectra of the complexes inputting a coordination of the azomethine nitrogen to the metal ions. The broad band at 3466 cm^{-1} for phenolic OH on the spectrum of the ligand disappeared for a weak node at lower frequencies at 3296-3510 cm^{-1} in the complexes. This also suggests the deprotonation and subsequent coordination of the oxygen atom of the phenolic group to the metal ions. The bands between 471- 722 cm^{-1} assigned to the M-N, band at 403-435 cm^{-1} for M-O stretching vibrations while bands

at 400 and 401 cm^{-1} were due to M-S, suggesting coordination. The ligand ISVN is therefore bidentate in nature. These results and their assignments are in good agreement with many reported literature [11,16,17,18].

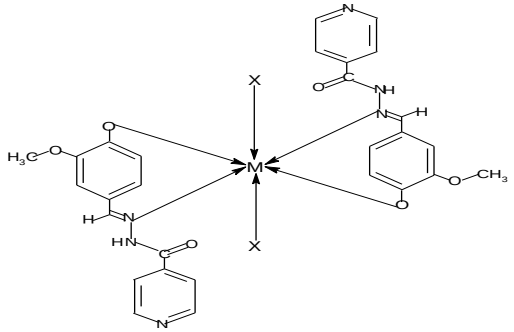
Electronic spectra

The electronic spectral data of the complexes are represented in Table 2. In the ligands, the band appearing in the 30674cm^{-1} range is assigned to the azomethine chromophore π- π* transition. Bands at higher energies 40,160cm^{-1} are attributed to n- π* transition due to the benzene ring delocalization of electrons. In the complexes, the azomethine chromophore shifted in the spectra of the complexes indicating that the imino nitrogen is involved in coordination to the metal ion. The electronic spectra of $[Co(ISVN)_2(A)_2]$ gave three absorptions within the range 23,201-24,937 cm^{-1} assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{2g} \rightarrow {}^4A_{2g}$ and $^4T_{1g}(P) \rightarrow {}^4A_{2g}$ transitions, typical of octahedral cobalt(II) complexes. (Jarad *et al.*, 2018, Iniama et al., 2 018[b]). Zn(II) is a d10 ion with completely filled d-orbitals hence the ground term symbol shows no splitting. It is diamagnetic [20]. The electronic spectra of Zn(II) complexes gave a band at 22,831 - 24,330 cm^{-1} due to ligand- metal charge transfer for which octahedral geometry was proposed [19,21].

The antimicrobial analysis

The results of the antibacterial and antifungal screening of the compounds indicated that the cobalt complex gave better inhibition zones than the streptomycin and fluconazole while the zinc complexes gave results comparable with streptomycin and fluconazole. The results also indicated that the complexes were bactericidal and fungicidal indicating that they can serve as raw materials for new drug production because the experimental result clearly indicated that at a minimum concentration of 2.5 to 5.0mg/ml a broad spectrum of microbes can successively be eliminated

Proposed structure for the complexes



Conclusion

The ligand and mixed ligand complexes were synthesized by simple condensation reaction at room temperature. The infrared and uv-visible spectroscopy revealed the bidentate coordination modes of the primary ligand to the metal ions. The compounds from analysis have very good antimicrobial properties.

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