

SYNTHESIS AND CHARACTERIZATION OF MIXED 1-10 PHENANTHROLINE AND VANCOMYCIN LIGANDS – METAL (II) COMPLEXES.



ISSN: 2141 – 3290

www.wojast.com

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ABSTRACT

Some metal (II) mixed ligand complexes were synthesized and characterized. The mixed ligands used were: 1, 10 - Phenanthroline and Vancomycin Hydrochloride. Three transition metal (II) chlorides were used (Cu, Mn, Zn). The synthesized complexes were characterized by solubility in six different solvents. Standard instruments were used for melting point and conductivity measurements while UV/Visible and Atomic Absorption Spectroscopy were used for spectroscopic studies. The result of the spectroscopic studies revealed that 1, 10 - phenanthroline is a bidentate ligand, coordinating through the pyridinic Nitrogen, while Vancomycin Hydrochloride coordinated through the Nitrogen of the primary amine and a hydroxyl group. The synthesized complexes are hexadentate.

INTRODUCTION

The question on the involvement of metal - ligand complexes in medicinal chemistry is of special interest. It is evident from previous studies that attaching organic drugs to metal containing fragments could enhance their activities (Ajibola, 1990). The use of metal complexes capable of enhancing biological activity has become a vibrant and growing area of research among inorganic chemists and biologists over the last few decades resulting in a variety of exciting and valuable drugs which are already in the market. (Bledsoe, 2005). Phenanthroline is commonly used in the formation of different complexes with a general variety of transition metals. (Ito, 2002) (Roestenbery, 2009).

Bipyridine and analogous ligands such as phenanthroline are commonly used in the formation of different complexes with a general variety of transition metals. These studies are important in understanding electron transfer processes, mixed valence complexes, magnetic coupling and magnetic transition. The photochemistry of the compounds owing to an extended π - system, non-covalent π interactions in biological process can also be mimicked. (Vahid *et al*, 2007).

This research work synthesised and characterised some mixed ligand - metal (II) complexes by using mixed ligands of 1,10 - phenanthroline and Vancomycin Hydrochloride with metal chlorides of Cu, Mn and Zn.

MATERIALS AND METHOD

Routine laboratory research apparatus were used. The drugs, chemicals and solvents used in this study were of high purity and were used as purchased from Sonitex Nigeria Enterprise without further purification.

Synthesis of the complexes

The following methods were employed in the synthesis of the complexes:

The single ligand-metal complexes were synthesised as described by (Adeyemo *et al*, 1983).

Synthesis of [Cu(Phen) (Van) Cl₂] H₂O

A solution of CuCl₂. 2H₂O (0.51g, 0.003mole) in distilled water (30mL) was added to a solution of 1, 10 – phenanthroline (0.59g, 0.003 mole) in 30mL of distilled water, The mixture was heated in a water bath for 5 minutes and Vancomycin (0.93g, 0006mole) also in 30mL distilled water was slowly added. The resulting mixture was stirred and heated in a water bath for 1 hour, until green coloured precipitates were formed. When there was complete precipitation, the mixture was cooled to room temperature. The green precipitate was filtered and dried at room temperature. The percentage yield was 83.00%.



The same method was applied for [Mn (phen) (Vanco) Cl₂] H₂O and Zn (phen) (Vanco) Cl₂] H₂O complexes.

RESULTS AND DISCUSSION

Some physical and spectroscopic data of the ligands and their metal complexes are presented in the tables below.

Table 1: Solubility determination for ligands and their metal complexes.

COMPOUND	Dist. H ₂ O		Ethanol		Methanol		Acetone		Chloroform		DMSO	
	C	H	C	H	C	H	C	H	C	H	C	H
1, 10-phenanthroline	NS	S	S	S	S	S	S	S	SS	S	S	S
Vancomycin Hydrochloride	SS	S	SS	S	SS	S	NS	NS	S	S	S	S
Mn (phen) (vanco) Cl ₂	SS	S	NS	SS	NS	S	NS	SS	NS	SS	SS	S
Zn (phen) (Vanco) Cl ₂	SS	S	SS	S	NS	SS	NS	SS	NS	NS	SS	S
Cu (phen) (vanco) Cl ₂	SS	SS	NS	SS	NS	SS	SS	SS	NS	SS	SS	S

Key: C-Cold, H-Hot, S-Soluble, SS-Slightly Soluble and NS-Not Soluble

Most of the complexes were soluble in the various solvents but showed variable solubilities in their cold solvents.

Table 2: Results of the physical properties of mixed ligand-metal complexes.

Compound	Colour	Melting Point (°c)	Conductivity (Cm ² mol ⁻¹)	% Yield
1, 10-phenanthroline	White	215	125	-
Vancomycin Hydrochloride	White	241	241	-
Mn (phen) (vanco) Cl ₂	Yellow	>300	65	73
Xn (phen) (vanco) Cl ₂	Grayish	198	114	57
Cu (phen) (vanco) Cl ₂	Green	>300	09	83

All the complexes except [Zn (phen) (vanco)] Cl₂ showed higher melting points compared with the individual ligands used in complex formation. The ligands showed a higher conductivity value than all the complexes. Most of the complexes were obtained as crystals apart from those from CuCl₂ salt which were in powder form.

Infrared spectra of mixed ligand-metal complexes.

The selected IR data for the mixed 1, 10-phenanthroline and Vancomycin metal-complexes and their ligands are presented in the Table 3. IR spectra of 1, 10-phenanthroline comprised of different functional groups as shown in Table 3. However, the absorption band with peaks at 1647.26 cm⁻¹ corresponding to ν(C=N) vibration and 1346.36 cm⁻¹ corresponding to ν(C-N) band in the ligand spectrum shifted to a lower frequencies. These were considered as the possible points of coordination to the metal ion centre. (Vagid *et al*, 2007).

Table 3: Selected IR data (cm⁻¹) for mixed 1, 10-phenanthroline-vancomycin metal complexes.

COMPOUND	V(N-H)	V(C-N)	Aromatic substituted benzene V(C-H)	Aromatic V(C=C)	V(C-Cl)	V(C=Cl)	V(C=O)	V(C=N)	Aromatic Ring	V(O-H)	V(C-O)
1, 10-phenanthroline	3649.44 (m)	1346.36 (m,s)	3061.13 (s)	1587.47 (s)	-	-	-	1647.26 (s)	779.29	3441.12 (b)	-
Vancomycin Hydrochloride	3853.90 (m)	1396.51 (m, s)	3064.99 (w)	1589.40 (m)	-	-	1772.64 (s)	1670.41 (w,s)	761.91 (s)	3736.24 (m)	1230.63 (s)
Mn (phen) (vanco) Cl ₂	3443.05 (b)	1342.50 (s)	3010.98 (s)	1589.40 (s)	418.57 (s)	852.56 (s)	1836.29 (m)	1622.19 (s)	719.47 (s)	3443.05 (b)	1257.63 (m)
Zn (phen) (vanco) Cl ₂	3790.25 (w)	1309.71 (m)	3051.49 (s)	1583.61 (s)	428.21 (s)	854.49 (s)	1656.91 (w)	1624.61 (s)	727.19 (s)	3437.28 (b)	1257.63 (w)
Cu (phen) (vanco) Cl ₂	3356.25 (b)	1313.57 (s)	3061.13 (s)	1587.47 (s)	422.42 (w)	850.64 (s)	1653.05 (s)	1653.05 (s)	723.33 (s)	3396.76 (b)	-

Note: S-strong, m-medium, w-weak, b-broad.

The ligand vancomycin hydrochloride also showed different absorption bands but the band that peaked at 3853.90 cm⁻¹ assigned to v(NH) stretch in the ligand shifted to a lower frequency in the complex. The peak at 3443.05 cm⁻¹ assigned to v(O-H) band in vancomycin shifted to a lower frequency in the complex. This an indication that vancomycin coordinated with the metal centre via these two functional groups. (Ajibade *et al.*, 2008).

From the IR data of the complexes the functional groups indicated in the ligands are also present in the complexes, but in the complex Mn (phen) (vanco) Cl₂, the V(N-H) band of 3853.90 cm⁻¹ had disappeared and now appeared at 3377.47 cm⁻¹ while the V(O-H) band which appeared at 3441.12 cm⁻¹ now shifted in the complexes to 3377.47 cm⁻¹ indicating coordination site.

The IR spectra of the complexes Zn (phen) (vanco) Cl₂ and Cu (phen) (vanco) Cl₂ when compared with the 1, 10-phenanthroline ligand showed that the C=N and C-N vibrations has shifted from 1647.26 cm⁻¹ and 1346.36 cm⁻¹ to 1622.19 cm⁻¹ and 1309.71 cm⁻¹ respectively indicating coordination positions to the metal.

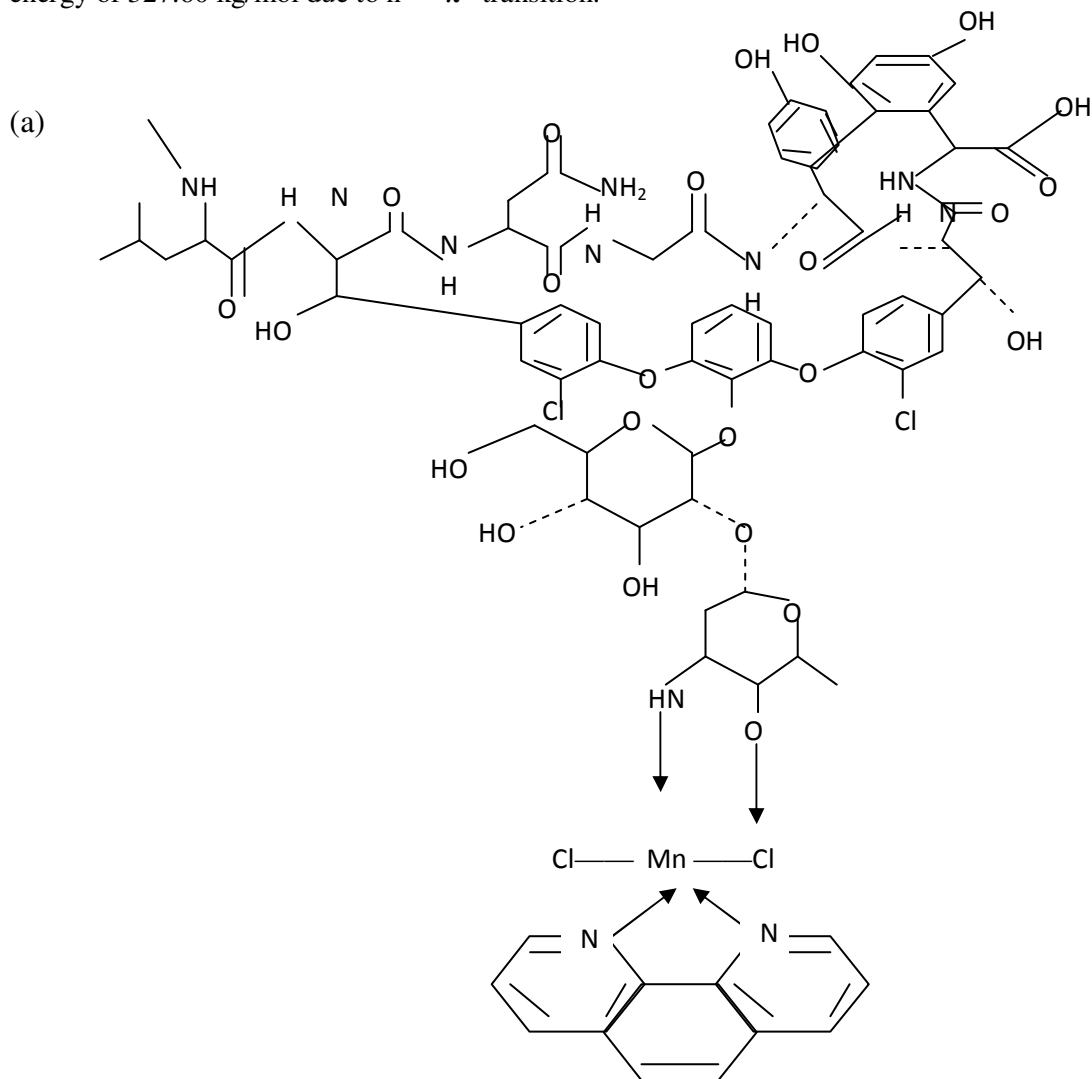
A comparison of the IR of the vancomycin Hydrochloride ligand with the complexes Mn (phen) (vanco) Cl₂, Zn (phen) (vanco) Cl₂ and Cu (phen) (vanco) Cl₂ indicated that the V(NH) stretch in the ligand undergoes a shift in the complexes from 3853.90 cm⁻¹ to 3443.05 cm⁻¹, 3443.05 cm⁻¹ and 3437.26 cm⁻¹, also the V(O-H) band in the ligand undergoes a shift in the complexes from 3443.05 cm⁻¹ to 3377.47 cm⁻¹, 3437.26 cm⁻¹ and 3358.25 cm⁻¹ to a lower frequency in the complexes suggested that (N-H) and (OH) group are involved in bonding to the metal ion. (Kalsi, 2005).

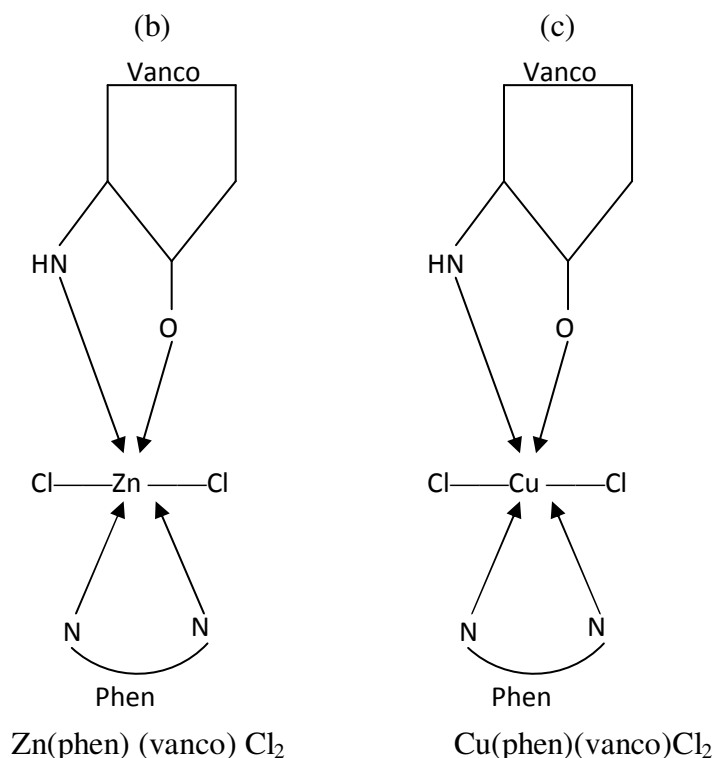
Results of Uv-visible spectroscopy of mixed 1, 10-phenanthroline and vancomycin metal complexes are presented in Table 4.

Table 4: Uv-visible spectra data of mixed 1, 10-phenanthroline and vancomycin complexes and their ligands.

Compound	Wavelength (nm)	Energies (kg/mol)	Assignment
1, 10-phenanthroline	191.44	625.28	$\pi \rightarrow \pi^*$
Hydrate	287.00	417.09	$n \rightarrow \pi^*$
Vancomycin	191.60	624.76	$\pi \rightarrow \pi^*$
Hydrochloride	365.40	327.60	$n \rightarrow \pi^*$
Mn (phen) (vanco) Cl ₂	195.50	612.30	$\pi \rightarrow \pi^*$
	280.50	426.75	$n \rightarrow \pi^*$
	599.50	206.05	LMCT
Zn (phen) (vanco) Cl ₂	311.00	384.90	$n \rightarrow \pi^*$
Cu (phen) (vanco) Cl ₂	198.00	604.57	$\pi \rightarrow \pi^*$
	307.50	389.28	$n \rightarrow \pi^*$
	567.00	211.12	LMCT

The ultraviolet spectrum of the 1, 10-phenanthroline hydrate showed two absorption peaks, one at 191.44 nm involving energy of 625.28 kg/mol due to $\pi \rightarrow \pi^*$ transition and the other at 287.00 nm involving energy of 417.09 kg/mol due to $n \rightarrow \pi^*$ transition. While the vancomycin Hydrochloride hydrate ligand also showed absorption peaks; one at 191.60 nm involving energy of 624.76 kg/mol due to $\pi \rightarrow \pi^*$ transition and the second peak at 365.40 nm involving energy of 327.60 kg/mol due to $n \rightarrow \pi^*$ transition.





Comparing the transitions in ligands and those of the complexes; Mn (phen) (vanco) Cl₂, Zn (phen) (vanco) Cl₂ and Cu (phen) (vanco) Cl₂ in $\pi \rightarrow \pi^*$ transitions there is a bathochromic shift or red shift (from shorter wavelength to a longer wavelength). On the contrary in $n \rightarrow \pi^*$ transition there is hypsochromic shift or blue shift (from a longer wavelength). (Olajire, 2011). This shift in the metal complexes is due to complexation (Ajibada et al, 2006). Again in the ligands, there is no Ligand Metal Charge Transfer (LMCT) transition but in the complexes excluding Zn (phen) (vanco) Cl₂ the other two complexes showed an LMCT transition also referred to as dd transition, indicating that there is complexation. (Simo *et al*, 2000).

CONCLUSION

Previous research has shown that complexing drugs to metal ions would enhance their activity. (Collins, 1980, Obaleye, 1989, Mohammed and Abdel-wenab, 2005). The complexes were characterized by melting point, conductivity measurements, infrared, Uv/visible and atomic absorption spectroscopy analysis. The results of the spectroscopic studies revealed that 1,10-Phenanthroline is a bidentate ligands and are coordinated to the metal ions through (Pyridine) Nitrogen, while Vancomycin Hydrochloride coordinated to the metal ion through the oxygen of the hydrozyl group and nitrogen of the secondary amine. The tentative metal ligand (M-L) assignments from all the spectroscopic data favour six coordination for the complexes studied.

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