



Synthesis and Characterization of Mixed 1, 10 – Phenanthroline and Ascorbic Acid Metal Complexes

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Abstract Giant biological molecules existing in living organism such as DNA possess metal binding sites. Hence, metal ion in metal complexes can interact with them, this account for their great impact in pharmaceuticals. Metal ion coordinated to drugs have been used to control toxicity and improve efficiency. The aim of this work was to synthesize and characterized mixed ligand metal (II) complexes of 1,10-Phenanthroline and L-Ascorbic acid coordinated to four transition metal (II) chlorides (Cu, Mn, Ni, Zn). The synthesized complexes were characterized by infrared spectroscopy, UV - visible, atomic absorption spectroscopy, conductivity measurement, solubility test and melting point. The result shows that the mixed ligand metal complexes were successfully synthesized. 1, 10 - phenanthroline is a bidentate ligand, coordinating through the nitrogen of the pyridine, and L-Ascorbic acid is coordinating through two hydroxyl group. The metal atom is proposed to coordinate to the two ligands with six bonds, hence a hexadentatetopology is recommended.

Keywords Synthesis, 1,10-Phenanthroline, Ascorbic Acid, Complexes

1. Introduction

The prevalence antimicrobial resistance among pathogenic bacterial is increasing both among hospital patients and in the community [1]. Generally, metal ions have lesser number of electrons than required for stability hence they are tagged electron deficient whereas, majority of biological molecules for instance protein DNA, drugs, are electron rich. This account for the interaction between metal ions and biological molecules. Designing and synthesizing metal-based drugs has been a growing area of research [2-4]. Different metals have been used in this regard ranging from platinum, to ruthenium, osmium, iridium, chromium, magnesium, calcium, nickel, silver and a host of others [5-11]. These metals containing medicine has found application as anticancer [8, 12], antibiotics [13], antimalarial [6], antiprotozoal studies [14]. Metal ion has been used to either improve the therapeutic or diagnostic efficiency of drugs [15]. They have also been used for drug delivery [16-17]. Another uniqueness of these metals complexation to drugs is to increase stability and reduced toxicity in such drugs.

In terms of its coordination properties, 1, 10-Phenanthroline is heterocyclic organic compound that form variety of strong complexes with transition metal ion [18-19]. Infant it is a building block for metals [20]. Ascorbic acid on the other hand is a naturally occurring organic compound with antioxidant properties [21], it is a white solid but impure



sample can appear yellowish, it dissolves well in water to give mildly acidic solutions. Being derived from glucose, many animals are able to produce it, but humans require it as part of their nutrition. This study is necessary in understanding electron transfer, various transition mechanisms that take place in biological molecules and how they can be simulated.

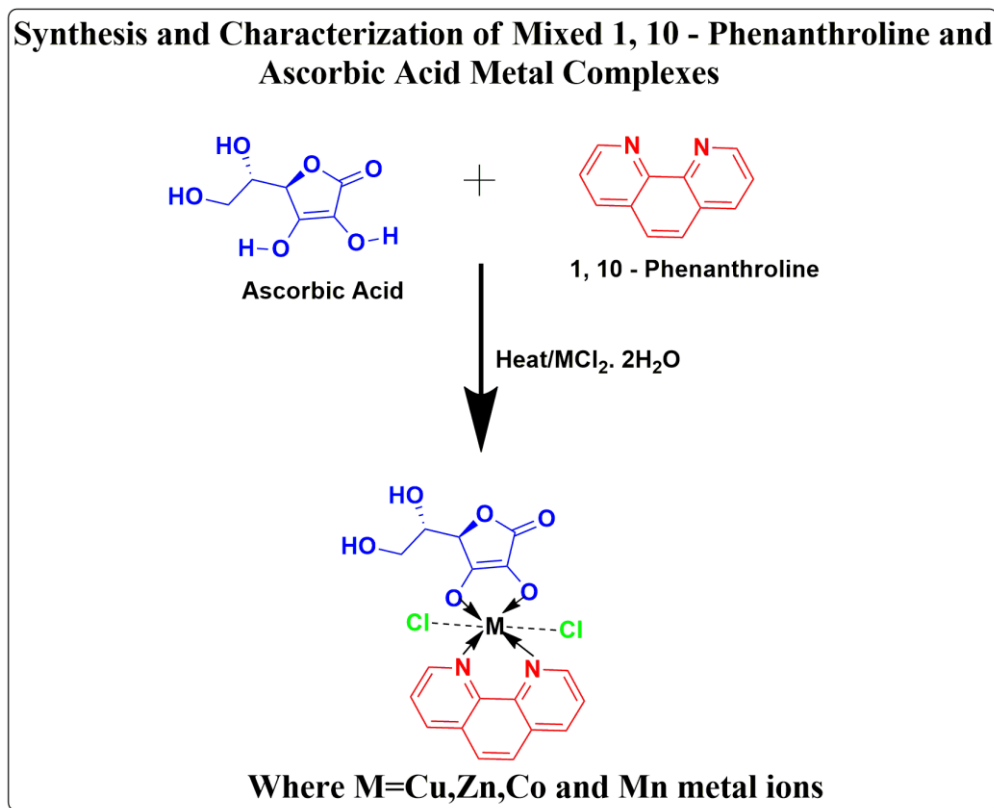


Figure 1: Graphical Abstract of the Synthesis and Characterization

2. Materials and Methods

Reagents: drugs, metals, solvents, and other chemicals used for this work were of high purity and were used as purchased from Sonitex Nigeria Enterprise without further purification.

3. Experimental

3.1. Synthesis of $[\text{Cu}(\text{phen})(\text{AscoCl}_2)]\text{H}_2\text{O}$

The mixed ligand metal complexes were synthesized with respect to the method described in the literature [22-23]. 530mg equivalent to 0.003mole of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 30mL of distilled water. A separate solution of 1, 10-phenanthroline was prepared by dissolving 590mg which is equal to 0.003mole in 30mL of distilled water. The two solutions were added together and heated for 5 minutes. A solution of Ascorbic acid 530 mg, = 0003 mole dissolved in 30mL of distilled water was then added and further heated for another 1 hour in a water bath. The mixture was transfer to an ice bath, which after cooling formed a green precipitant that was filtered and dried at room temperature. The percentage yield is 15%. The same method was used for Mn, Ni, and Zn metal complexes *via* their respective $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ salts respectively.



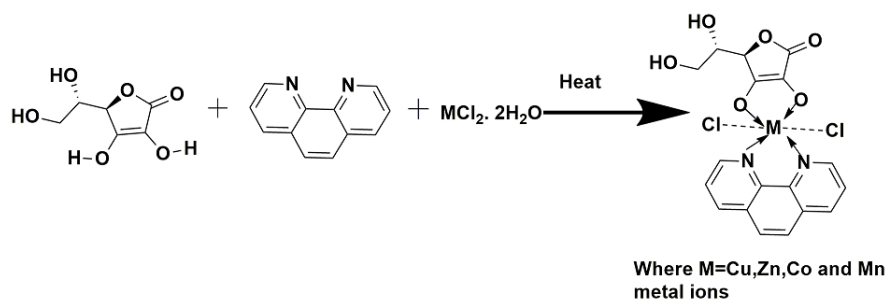


Figure 2: Reaction scheme of the complexes

4. Results and Discussion

The result of some physical properties and spectroscopic data of the ligands and their metal complexes are presented in tables

Table 1: Solubility test for mixed 1,10 – phenanthroline and Ascorbic acid 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
Penicillin G	S	S	S	S	S	S	SS	SS	NS	SS	SS	S
Co(phen) (pen) Cl ₂	SS	S	NS	SS	S	S	NS	SS	S	S	S	S
Zn (phen) (pen) Cl ₂	NS	SS	NS	SS	NS	S	SS	SS	NS	NS	S	S
Mn (phen) (pen) Cl ₂	SS	S	SS	SS	SS	S	NS	SS	NS	NS	SS	S
Cu (phen) (pen) Cl ₂	SS	S	SS	SS	SS	SS	NS	S	NS	NS	NS	SS

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 solubility in their cold solvents.

Table 2: Analytical data of mixed 1, 10 phenanthroline and Ascorbic acid metal complexes

Compound	Colour	Melting Point (°C)	% Yield	Conductivity (µs/cm)
1,10-Phenanthroline	White	125	-	01
Ascorbic Acid	White	204	-	29
Cu (Phen) (Asco)Cl ₂	Green		15.00	64
Zn (Phen) (Asco) Cl ₂	Grey	>300	87.44	125
Co (Phen) (Asco) Cl ₂	Clay	> 300	12.02	01
Mn (Phen) (Asco) Cl ₂	Yellow	>300	92.98	48

All the complexes showed higher melting points compared with the individual ligands used in complex formation. With exception of Co(Phen) (Asco) Cl₂. All the other complexes showed a higher conductivity values then the ligands except Co (Phen) (Asco) Cl₂ complex. Apart from Cu (Phen) (Asco)Cl₂ all the other complexes were obtained as crystals. The complexes were of various colours.

Table 3: Selected IR data (cm⁻¹) of 1, 10-phenanthroline and Ascorbic acid metal complexes

Compound	V(N-H)	V(C-N)	Aromatic substitute benzene VCC-H	Aromatic V(C=C)	V(C=O)	V(C=N)	Aromatic Ring	V(O-H)	V(C-O)	V(M-L)	V(C-CL)
1,10-Phenanthroline	3849.44 (m)	1346.36 (m,s)	306 1.13 (s)	1587.47 (s)	-	1647.25 (s)	779.29 (s)	-	-	-	-
Ascorbic Acid	-	-	3030.27 (b)	1541.18 (m)	1753.35 (s)	-	756.12 (s)	3649.44 (m)	1276.91 (s)	-	-
Cu (phen) (Asco) Cl ₂	3362.04 (w)	1311.64 (w)	3053.42 (s)	1585.54 (s)	1967.48 (s)	1626.05 (s)	723.33 (s)	3439.19 (b)	1222.91 (s)	430.14 (s)	854.49 (s)
Zn (phen) (Asco) Cl ₂	3390.97 (b)	1309.71 (m)	3051.49 (s)	1583.61 (s)	1791.93 (s)	1624.12 (s)	725.26 (s)	3508.63 (b)	1224.84 (s)	428.21 (s)	852.56 (s)
Co (phen) (Asco) Cl ₂	3064.99 (s)	1313.57 (s)	3064.99 (s)	1518.03 (s)	1905.73 (s)	1612.54 (s)	727.19 (s)	3414.12 (b)	1226.77 (m)	424.35 (s)	852.56 (s)
Mn (phen) (Asco) Cl ₂	3394.63 (b)	1342.50 (s)	3051.49 (s)	1572.04 (s)	1834.36 (m)	1622.19 (s)	719.47 (s)	3394.63 (b)	1257.63 (s)	418.57 (s)	852.56 (s)



The IR data of 1, 10- Phenanthroline and Ascorbic acid were compared with their metal – complexes. The $\nu(\text{C}=\text{N})$, 1647.25cm^{-1} band of the 1, 10-Phenanthroline molecule undergoes a shift in all the complexes. The observed values agree with previous report of 1, 10-Phenanthroline complexes [24].

The $\nu(\text{O}-\text{H})$ band in the Ascorbic acid also shifted to a lower frequency in all the complexes. These also could be attributed to a coordination site. Again, the $\nu(\text{C}=\text{O})$ disappeared in most of the complexes.

In the Cu (Phen) (Asco) Cl_2 complex there is a shift of the $\nu(\text{C} = \text{N})$ vibration band from 1647.26cm^{-1} to 1626.05cm^{-1} , $\nu(\text{C}-\text{N})$ vibration band; 1348.36 to 1311.64 . While $\nu(\text{O}-\text{H})$ shifted from 3649.44cm^{-1} to 3439.19 and $\nu(\text{C}=\text{O})$ which is 1753.35 disappeared. This is attributed to the formation coordination bond between the metal and the ligand [25].

Also, in the Zn (Phen) (Asco) Cl_2 , complex the $\nu(\text{C}=\text{N})$ vibration shifted from 1647.26cm^{-1} to 1624.12cm^{-1} and $\nu(\text{C} - \text{N})$ from 1346.36 to 1309.71cm^{-1} from 1, 10-Phenanthroline. The O-H from Ascorbic acid vibration shifted from 3649.44 to 3508.63 indicating coordination site. For Co (Phen) (Asco) Cl_2 , the $\nu(\text{C} = \text{N})$ shifted from 1647.26cm^{-1} to 1612.54cm^{-1} and the $\nu(\text{C}-\text{N})$ vibration from 1346.35cm^{-1} to 1313.57cm^{-1} for the 1, 10-Phenanthroline indicating coordination site. Also the $\nu(\text{O}-\text{H})$ shifted from 3649.44 to 3414.12cm^{-1} and the $\nu(\text{C}=\text{O})$ vibration band of 1753.35 also disappeared also indicating coordination site for Ascorbic acid.

For Mn (Phen) (Asco) Cl_2 , complex the $\nu(\text{C}=\text{N})$, 1346.36cm^{-1} to 1342.50cm^{-1} for the 1,10 – Phenanthroline ligand indicating coordination site. The O-H shifted from 3649.44 to 3394.63 and the CO also disappeared for the Ascorbic acid indicating coordination site [25].

Table 4: Some selected UV-visible spectral of mixed 1, 10-phenanthroline and Ascorbic acid metal complexes

Compound	Wavelength (nm)	Energies (KJ/mol)	Assignment
1, 10-phenanthroline	191.40	625.49	$\pi \rightarrow \pi^*$
	286.20	418.25	$n \rightarrow \pi^*$
Ascorbic Acid	192.40	622.16	$\pi \rightarrow \pi^*$
	282.40	417.80	$n \rightarrow \pi^*$
Cu (phen) (Asco) Cl_2	230.50	519.32	$\pi \rightarrow \pi^*$
	310.00	386.14	$n \rightarrow \pi^*$
	542.50	220.65	LMCT
Zn (phen) (Asco) Cl_2	216.50	552.91	$\pi \rightarrow \pi^*$
	311.50	384.28	$n \rightarrow \pi^*$
	471.00	254.15	LMCT
Co (phen) (Asco) Cl_2	225.00	532.02	$\pi \rightarrow \pi^*$
	316.00	378.47	$n \rightarrow \pi^*$
	449.00	266.60	LMCT
Mn (phen) (Asco) Cl_2	225.00	532.02	$\pi \rightarrow \pi^*$
	286.50	417.81	$n \rightarrow \pi^*$
	539.00	222.08	LMCT

To further confirm the synthesized mixed ligand metal complexes, the complexes were characterized by UV-visible. The result from the UV data shows that, 1, 10-phenanthroline shows two absorption band at 191.40 nm (625.49 kJ/mol) and 286.20 nm (418.25 kJ/mol) due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Similarly, Ascorbic acid shows two absorption band at 192.40 nm (622.16 KJ/mol) and 282.80 nm (423.28 KJ/mol) due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition. The complexes show bands between 225.00 - 539.50 nm. Cu (phen) (Asco) Cl_2 showed a definite band at 542.50nm assigned to ligand metal charge transfer (LMCT), Zn (phen) (Asco) Cl_2 with a band at 471.00nm, Co (phen) (Asco) Cl_2 at 449.00 nm and Mn (phen) (Asco) Cl_2 at 539.00 nm. Basically, all the complexes showed characteristic bands which are assigned to metal to ligand charge transfer (MLCT) transitions from the filled 3d orbital to the empty π^* orbital ($d\pi-\pi^*$) as observed in the spectra of related complexes with N,N bidentate ligands. The bands have undergone bathochromic shift in all the complexes due to complexation. The bathochromic shifts observed can be attributed to change in the compound composition [26].



LMCT absorption transitions were observed in the mixed complexes. These shows that complexation has occurred in the metal complexes [27]. In the ligands there is no LMCT (Ligand Metal Charge Transfer) but present in all complexes indicating a dd transition, by implication complexation. The observed absorption in the visible region in all the mixed ligands metal complexes that resulted to the d-d transition is an indication that the ligands coordinated to the metals as expected as an evidence of real complexation.

4.1. Atomic Absorption Spectroscopy

The technique used for the determination of the present of metals in the samples is the one recommended by Yan, Sperling, & Welz, [28] which is supported by Beer Lambert's law. The digestion and dilution were done with respect to double acid method.

Table 5: The atomic absorption spectroscopy data of mixed 1, 10-phenanthroline and Ascorbic acid metal complexes

Metals Analyzed	Concentration ($\mu\text{g/g}$)
Copper	158.14
Zinc	171.89
Cobalt	96.14
Manganese	214.63

The atomic absorption spectroscopy result revealed the presence of each of the metals in their respective mixed ligand metal complexes in good concentration, with copper having a concentration of 158.14, Zinc =171.89, Cobalt = 96.14 and Manganese = 214.63 having the highest.

4.2. Proposed structure for the mixed 1,10-phenanthroline and L-ascorbic acid metal complexes.

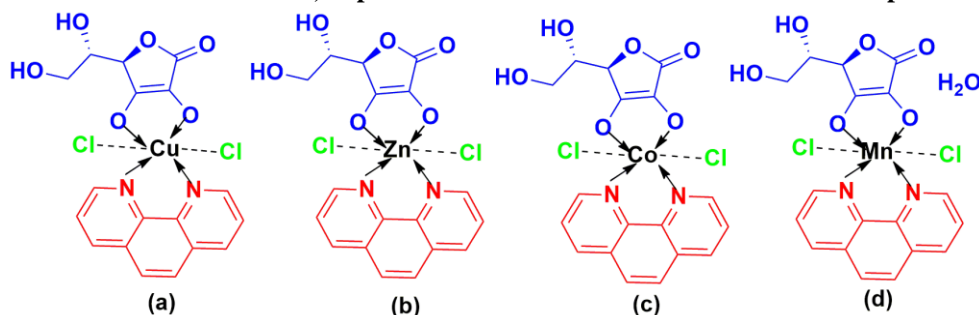


Figure 3: The proposed structures of (a) $\text{Cu}(\text{Phen})(\text{Asco})\text{Cl}_2$, (b) $\text{Zn}(\text{Phen})(\text{Asco})\text{Cl}_2$, (c) $\text{Co}(\text{Phen})(\text{Asco})\text{Cl}_2$ and (d) $\text{Mn}(\text{Phen})(\text{Asco})\text{Cl}_2$.

5. Conclusion

This research work deals with the synthesis and characterization of mixed ligands metal complexes. The aim of which is to contribute to efforts being made to explore novel complexes with new mechanism of operation that can be used against resistant pathogens. The complexes $\text{Cu}(\text{Phen})(\text{Asco})\text{Cl}_2$, $\text{Zn}(\text{Phen})(\text{Asco})\text{Cl}_2$, $\text{Co}(\text{Phen})(\text{Asco})\text{Cl}_2$ and $\text{Mn}(\text{Phen})(\text{Asco})\text{Cl}_2$ have been synthesized and characterized. Their structures have been inferred from the infrared spectroscopy, UV-visible, atomic absorption spectroscopy, conductivity measurement, solubility test and melting point. All complexes studied favours six coordination bonds, hence they were proposed to be hexadentate. The 1,10-Phenanthroline is bidentate ligand and is coordinated to the metal ions via the (Pyridine) nitrogen. While the Ascorbic acid coordinated to the metal ion through the oxygen of the hydroxyl group.

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