Spectroscopic Study of Metal (II) Complex of Sulphamethazine with 1,10 Phenanthroline

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Abstract:
As part of the current research for more effective antimalarial drug, Cu (II) complex of sulphamethazine with 1,10 phenanthroline was synthesized. The novel complex was characterized by Elemental analysis, FT-IR and electronic spectroscopy. The novel complex is insoluble in water, which is an indication of covalent and non- electrolyte character. The elemental analysis result of the complex correspond with the proposed formula $[Cu(SUF)(phen)(SCN)_2]$. The electronic spectrum of sulfamethazine and 1, 10- phen showed absorption bands at 212 nm (47169 cm^{-1}) and 306 nm (32679 cm^{-1}). These bands were assigned to the n – δ* and π – δ* transitions. The infrared bands were seen at 3443 – 3344 cm^{-1} which were attributed to the presence of ν (NH_2), ν(NH) and ν(OH) vibrations experience bathochromic shift in the metal complex. The parent ligands acted as a bidentate chelating agent showing coordination through the pyridine nitrogen and the nitrogen of the NH moiety in this case.

Keywords: Sulphamethazine, metal – drug complex, ligand, spectroscopy, 1-10 phenanthroline.

1.0. Introduction:

The treatment of malarial was first attempted in the 17th century with the use of alkaloids obtained from the bark of the cinchona tree. Pierre Pelletier and Joseph Coventou French chemists in 1820 isolated and identified the most important alkaloids named quinine from the bark of cinchona tree [2, 12-16]. It still remains an active member of the antimalarial drugs manufactured today. Although, from current researches, the causative protozoa *Plasmodium falciparium* has posed resistance to the available antimalarial drugs [6, 7, 10] Sulpha drugs as well as the ligands derived from them have shown appreciable biological activity for a long time ago and their increase has been ascribed to their complexation to metal ions [1, 11, 21, 24]. Drug therapy is one of the main methods of malaria control. There are some drugs that affect different stages (exoerythrocytic, erythrocytic, and sexual) of the parasite's life cycle. For instance, chloroquine (CQ), mefloquine (MQ), amodiaquine (AQ), and halofantrine (HAL) are effective drugs in parasite's erythrocytic stage that interfere with detoxification mechanism of the parasite. These drugs belong to the family of quinolineanalogs. Actually, CQ and AQ are 4-aminoquinoline derivatives, whereas MQ and HAL are aryl-amino alcohols derivatives. All these drugs have already been used in malaria control, elimination, and eradication programs because of their easy usage, affordable synthesis, or great clinical efficacy. Some of them are also safe for children and pregnant women.

Nevertheless, in recent years, the value of these drugs for the prevention and treatment of malaria has decreased after development and the spread of drug resistance, especially against quinoline analogs. Drug development based on synthetic methods plays a vital role in modern drug discovery, and in this concern, the identification of lead compound is very important. For instance, chloroquine was designed and synthesized based on quinine, as an identified natural product, for the purpose of decreasing quinine side effects [14, 15, 26, 27]. Apart from their complexing ability, the metal-drug complex obtained from their coordination to the metal ions play significant roles in metabolic and toxicological function in the biological systems such as antibacterial and antifungal through exchanges of different functional groups without modification of the structural features [3, 14, 16]. Among the Nitrogen containing chiral ligands which have been discovered and found to be useful in its application in chemotherapy and asymmetric catalysis is 1,10 phenanthroline. One of the most interesting features of the drug – metal coordinated system is the concerted spatial arrangement of the drug (Ligands) around the metal ion [4, 5, 17-20]. The properties of the complexes (both redox and photochemical) which are gradually varied leads to appropriate substitution on the phenanthroline rings [8, 9, 22-25]. In this study, we present the spectroscopic analysis of the metal (II) complex of mixed Ligand Sulphamethazine mixed with 1,10 Phenanthroline.

2.0. Experimental method

2.1. Synthesis of Copper (II) Complex of Sulfamethazine with 1, 10 – Phenanthroline

$Cu(SCN)_2$ from $Cu(NO_3)_2.3H_2O$ 0.242 g (1 mmol) was obtained from the reported procedure in previous works. To the ethanolic solution a 0.198 g (1 mmol) of 1, 10-phenanthroline in 10 mL ethanol was added slowly and stirred only for 20 mins. The green coloured precipitate obtained was filtered, washed and dried over silica gel in a desiccator [17-19, 23].

3.0. Discussion

3.1. Mixed-Ligand Metal Complexes of Sulfamethazine with 1, 10-phenanthroline

The analytical data, UV-visible and FTIR results obtained are summarized in Tables 1,2 and 3 respectively. It is an amorphous powder with green colouration. Its melting point is higher than those of the ligands, this result showed confirmation with other research works [19, 22, 23]. The elemental analysis result of the complex correspond with the proposed formula: $[Cu(SUF)(phen)(SCN)_2]$. The (SUF)(phen) mixed-ligand complex consists of a molecule of SUF (coordinated to the metal through the N-atom of the NH_2 group) and one molecule of phen (coordinated the metal ion through the two N-atoms of the two rings). The complex is insoluble in the solvent used for the synthesis.

Table 1. Analytical data for mixed-ligand complex of Sulfamethazine with 1, 10-phenanthroline

S/N	Ligands/ Complexes	Appearance/ Colour	Yield %	Molecular Weight	Melting Point (°C)	% Elemental Analysis		
						C	H	N
1.	SUF	Amorphous Powder White	-	283.34	199			
2.	1,10-phen	Crystalline White	-	180.21	106			
3.	$[Cu(SUF)(phen)(SCN)_2]$	Powder Green	89	684.31	230.2	49.20 (49.14)	4.25 (4.12)	15.98 (16.37)

3.2. Electronic spectra of Mixed Sulfamethazine with 1, 10-Phenanthroline and Its Metal Complex

The UV-visible spectra data are shown in Table 2. The electronic spectrum of sulfamethazine and 1, 10- phen shows absorption bands at 212 nm (47169 cm^{-1}) and 306 nm (32679 cm^{-1}). These bands have been assigned to the n – δ* and π – δ* transitions. These transitions undergo a bathochromic shift in the metal complexes due to complexation. This is in agreement with other findings [10, 17]. In Cu(II) complex of (SUF)(phen), there are two bands found in the UV-region at 224 nm and 339 nm. These involve energies of 44642 cm^{-1} and 29498 cm^{-1} assigned to n – δ* and π – π* transitions respectively. This finding is not in agreement with the research work of Shahroosvand *et al* [23]. Copper has a spectroscopic ground term symbol of ^2D. The ^2D orbital is split in a tetrahedral field or in a distorted octahedral field into sub-energy levels $^2E \rightarrow {}^2T$ and $^2Eg \rightarrow {}^2T_2g$ respectively. There is one broad absorption band at 699 nm (14306 cm^{-1}) which is due to d – d transition $^2Eg \rightarrow {}^2T_2g$. Octahedral structure may be possible, though distorted, due to inherent Jahn-Teller effect on a d^9 system [18-20].

Table 2. Electronic Spectra Data of Sulfamethazine with 1, 10- phenanthroline Metal Complex

Compound	Electronic conf.	Wavelength nm (cm^{-1})	Assignment/Transition
Cu (SUF)(phen) $(SCN)_2$	d^9	224 (44642)	n – π*
		339 (29498)	π – π*
		699 (14306)	$^2Eg - {}^2T_2g$

3.3. FTIR Spectra of Mixed Sulfamethazine with 1, 10-phenanthroline and Its Metal Complex

The infrared spectrum datum of the ligands and its metal complex are recorded and compared in Table 3. Bands at 3443 – 3344 cm^{-1} that can be attributed to the presence of ν (NH_2), ν(NH) and ν(OH) vibrations experience bathochromic shift in the metal complex. The presence of isothiocyanate in the metal complex was seen in the region 2094 cm^{-1} in agreement with literature value as reported in other research works [19, 22-23]. The effect of the coordinated metal is noticeable on the SO_2 symmetrical and asymmetrical stretching modes that are shifted to lower wavenumbers. The region assigned to ν(C – N) has1437 cm^{-1} which represent a decrease in frequency of 12 cm^{-1} compared to the free ligands. This is a confirmation of a coordination site. The Cu – O is seen at the region of 530 cm^{-1}. These reports are similar to other research works [10, 14, 17-18].

Table 3. FTIR Frequencies (cm^{-1}) of Mixed Sulfamethazine with 1,10-Phenanthroline Metal Complex

SUF	Phen	Cu(SUFphen) $(SCN)_2$	IR Band assignment (KBr, Cm^{-1})
3443(asy)	3416(asy)	3452(asy)	ν (NH,NH_2)
3344(sym)	3387(sym)	3064(sym)	ν (NH,NH_2)
2352(m)	2359(w)	2094(s)	ν (NCS)
1639(s)	1647(m)	1624(w)	ν (C=O)
1595(s)	1504(s)	1581(m)	ν (C=N)
1437(s)	1423(s)	1425(s)	ν (C – N)
1147(s)		1136(m)	ν (S = O)
	624(w)	646	ν (C – S)
		530	M – O

$C_{28}H_{22}N_8O_3S_3Cu$

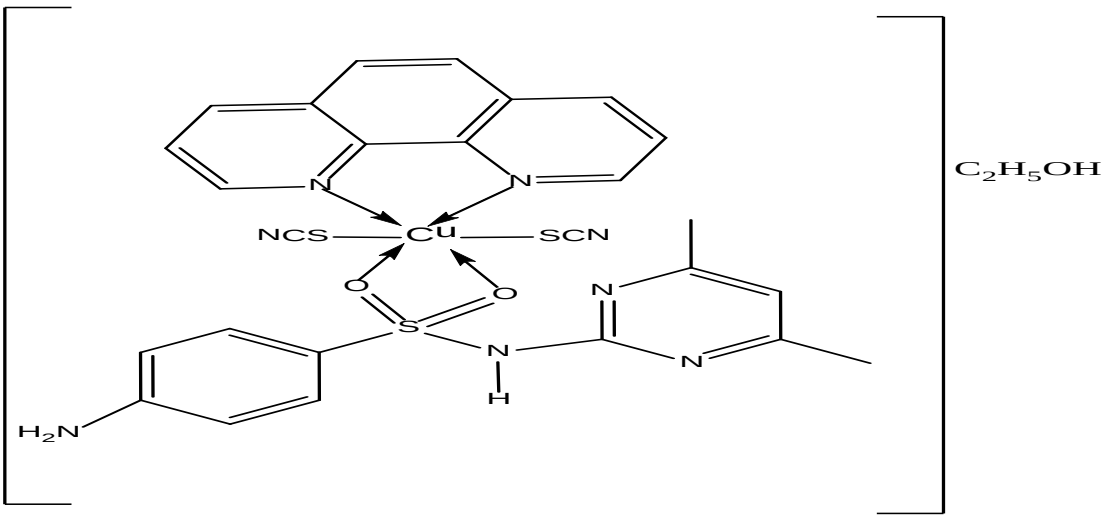

Figure 1. Proposed Structure of [Cu(SUFPHEN)$(SCN)_2$] C_2H_5OH

4.0. Conclusion

In the present study the two antimalarial drugs (Ligands) coordinated to the metal ion Cu (II) through the pyrimidine N- atom of the 1,10 phenanthroline, N and O functional groups of the Sulphamethazine with the two atoms of the thiocynate resulting in a 6 – coordinate geometry, Octahedral structure in conformation with the results obtained from the spectroscopic analyses of the proposed metal complex.

5.0. References

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