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Preparation and Evaluation of Mixed-Ligand Complexes of Cu (II) and Co (II) with Amodiaquine Hydrochloride and Sulphamethazine

***[1]ENEMOSE, EA; [2]AKPORHONOR, EE; [3]KPOMAH, B**

*[1]Department of Chemistry, School of Basic Sciences, Nigeria Maritime University, Okerenkoko, Delta State, Nigeria
[2]*Department of Chemistry, Faculty of Science, Delta State University, Abraka. Nigeria*
[3]*Department of Chemistry, School of Sciences, Delta State College of Education, Mosogar, Nigeria*
**Corresponding Author Email: tressurekpomah@yahoo.com*

ABSTRACT: Cu (ll) and Co (II) complexes of amodiaquine hydrochloride and sulphamethazine (AMOSUF) have been prepared and characterized by elemental analysis, molar conductivity, FTIR and electronic spectroscopy. The compounds are non-electrolyte in solution and the spectra data of the complexes are consistent with 6-coordinate octahedral complexes. It has been found that the two ligands behave as a bidentate forming 1:1:1 stoichiometry and octahedral geometry.

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The spread of resistant parasite strains to all kinds of drugs is growing high in tropical and sub-tropical regions, including Africa, Asia and part of America (Sachs and Malancy, 2002). Resistance results from a mutation in the parasite chromosome or the acquisition of extra – chromosomal DNA (Trampuz *et al.,* 2003).The efficacies of some therapeutic agents are known to increase upon coordination thus metal-based drug is seen as promising alternatives for possible replacement for some of the current drugs. Malaria was successfully reduced after World War II because of easy access to cheap insecticide and readily available drugs (Greenwood and Mutabingwa, 2002; World Health Report 2004; Tripathi *et al*., 2005; Ajibade and Kolawole, 2010). In the search for novel drug against resistant parasites, the use of metal complexes has received considerable attention in recent years (Delhaes *et al.,* 2001; Novarro *et al.,* 2004; Novarro *et al.,* 1997; Biot *et al.,* 1997; Blackie *et al.,* 2003). As part of our effort to develop metal based chemotherapy, we presented the preparation and study of mixed ligand complexes of amodiaquine hydrochloride mixed with sulphamethazine (Enemose, *et al.,* 2014).

MATERIALS AND METHODS

Synthesis of Copper (II) Complex of Sulfamethazine with Amodiaquine Hydrochloride: Cu $(NO_3)_2 .3H_2O$ 0.242 g (1 mmol) in 10 mL methanol was added drop wise to 0.278 g (1 mmol) sulfamethazine dissolved in 20 mL methanol which was stirred continuously for 1 h at 40 ^{O}C and a 20 mL methanolic solution of 0.356 g (1 mmol) of amodiaquine hydrochloride was slowly added. The dark brown precipitate obtained was filtered, washed thoroughly with methanol and dried in a desiccator over silica gel.

Synthesis of Cobalt (II) Complex of Sulfamethazine with Amodiaquine Hydrochloride: The procedure reported was followed to obtain $Co(SCN)_2$ from $[Co(NO_3)_2 . 6H_2O]$ 0.291 g (1 mmol). The complex was prepared by dissolving 0.278 g (1 mmol) of sulfamethazine in 20 mL ethanol followed by dropwise addition of the metal salt with continuous stirring for 1 h at 40^{O}C and to this solution a 20 mL ethanolic solution of 0.356 g (1 mmol) of amodiaquine hydrochloride was slowly added. The dark-green precipitate formed was refluxed for another 1 h and washed with ethanol. Filtrate was left for slow evaporation at room temperature. Both the product from the filtrate and precipitate were analysed to determine their composition. The precipitate was analysed pure.

RESULTS AND DISCUSSION

**Corresponding Author Email: tressurekpomah@yahoo.com*

Mixed-Ligand Metal Complexes of Sulfamethazine with Amodiaquine Hydrochloride: The result of the elemental analysis, UV-visible and infrared are summarized in Tables 1, 2 and 3 respectively. The elemental analysis results of the complexes are in agreement with the formula proposed: $[Cu(SUF)(AMQ)(NO_3)_2]$ and $Co(SUF)(AMQ)(SCN)_2$ which was further confirmed by the FTIR results of the complexes. The point of coordination of the ligands to the metal ion was through the N-atom of the C=N group of the SUF and also through the O-atom of the OH and the N-atom of the NH functional groups of the AMQ. From the solubility test, the complexes were practically insoluble in the original solvent (organic) used for the synthesis. Their melting points were quite different from those of the ligands.

Electronic spectra for Mixed Sulfamethazine with Amodiaquine Hydrochloride and Its Metal Complexes: The UV-visible data are shown in Table 2. The UV-spectrum of the free sulfamethazine and amodiaquine hydrochloride shows absorption bands at 212 nm to 948 nm. These transitions involve energies of 47169 cm^{-1} and 10548 cm^{-1}. These bands have been assigned n – π*, π – π* and d – d transitions. These bands undergo hypsochromic shift in the metal complexes due to complexation (Ajibade *et al.,* 2007). The Cu (II) complex of (SUF)(AMQ) showed a broad band at 23923 cm^{-1} expected for a d–d transition, $^{2}Eg \rightarrow {}^{2}T_{2}g$ of an octahedral Cu(II) complex (Greenwood, 1984). The broadness of the band could be attributed to the overlapping of several bands as a result of strong Jahn-Teller distortion expected in a d^9 ion. Two other bands appeared in the ultraviolet region at 209 nm (47846 cm^{-1}) and 282 nm (35460 cm^{-1}) assigned to n – π* transitions. The Co(II) complex of (SUF)(AMQ) gave two absorption bands in the UV region at 244 nm (40983 cm^{-1}) and 313 nm (31948 cm^{-1}) which is assigned to n – π* and π – π* respectively. However, two weak bands that peaked at 23148 cm^{-1} and 17921 cm^{-1} appeared in the visible region and were assigned to $^{4}T_{1}g \rightarrow {}^{4}T_{2}g$ and $^{4}T_{1}g \rightarrow {}^{4}A_{2}g$ respectively. However, other expected transitions for the complexes appear to have been obscured by the more intense transition because of their low intensity.

Table 1: Analytical data for mixed-ligand complexes of Sulfamethazine (SUF) with Amodiaquine hydrochloride (AMQ)

S/N	Ligands/ Complexes	Appearance/ Colour	Yield (%)	Molecular Weight (g/mol)	Melting Point (^{O}C)	Elemental Analysis (%)		
						C	H	N
1.	SUF	Amorphous Powder/ White	-	283.34	199			
2.	AMQ	Amorphous Powder/ Yellow	-	356.5	169			
3.	$[Cu(SUF)(AMQ) (NO_3)_2]$	Powder/Dark Brown	44	858.21	270. DT	43.11 (44.78)	4.48 (4.35)	14.73 (14.89)
4.	$[Co(SUF)(AMQ) (SCN)_2]$	Crystalline/ Sea-green	48	845.75	199	48.68 (48.28)	4.38 (4.41)	14.04 (14.09)

Table 2: Electronic Spectra Data of Sulfamethazine with Amodiaquine

Compound	Electronic conf.	Wavelength nm (cm^{-1})	Assignment/Transition
SUF		212 (47169)	n – π*
		268 (37313)	n – π*
		306 (32679)	π – π*
AMQ		223 (44843)	n – π*
		348 (28735)	π – π*
		948 (10548)	d – d
$Cu(SUF)(AMQ)(NO_3)_2$	d^9	209 (47846)	n – π*
		282 (35460)	n – π*
		418 (23923)	$^{2}Eg \rightarrow {}^{2}T_{2}g$
$Co(SUF)(AMQ)(SCN)_2$	d^7	244 (40983)	n – π*
		313 (31948)	π – π*
		432 (23148)	$^{4}T_{1}g \rightarrow {}^{4}T_{2}g$
		558 (17921)	$^{4}T_{1}g \rightarrow {}^{4}A_{2}g$

Table 3: IR Frequencies (cm^{-1}) of Mixed Sulfamethazine with Amodiaquine Metal Complexes

SUF	AMQ	$Cu(SUF)(AMQ) (NO_3)_2$	$Co(SUF)(AMQ) (SCN)_2$	IR Band Assignment (KBr, cm^{-1})
3443 asy	3417 asy	3450 asy	3443 asy	ν (OH), ν (NH_2)
3344 sym	3358 sym	3230 sym	3344 sym	ν (NH)
2352 (m)	2125 (m)		2089 (m)	(SCN)
1639	1618	-	1639	(νC=O)
1595	1587	1597 (s)	1597	ν (C=N)
-	1510	1500	1548	ν (C – O)
1437	1450	-		
1303	1367	1384	1342	ν(C – N)
1147	1163		1141	ν (S=O)
			680	(C – S)
		590	538	M – O
		428		M – N

FTIR Spectra of Mixed Sulfamethazine with Amodiaquine and Its Metal Complexes: The FTIR spectra data of Cu(SUF)(AMQ)$(NO_3)_2$ and Co(SUF)(AMQ)$(SCN)_2$ complexes of sulfamethazine with amodiaquine are recorded in Table 3, the bands in the region 3443 – 3358 cm^{-1} due to asymmetrical and symmetrical stretching modes of NH_2 in the spectrum of the ligands underwent appreciable change in the spectra of the complexes. Bands at 1367 – 1303 cm^{-1} in the ligands assigned to ν(C–N) which shifted appreciable in the complexes are also evidence as a site for coordination. In addition to the above discussed features, Co(SUFAMQ)$(SCN)_2$ showed a medium intensity frequency band at 2089 cm^{-1} attributed to ν(SCN) due to coordination to the metal ion. Bands at 590–538 cm^{-1} in the metal complexes are assigned for M – O and 428 cm^{-1} assigned for M–N.

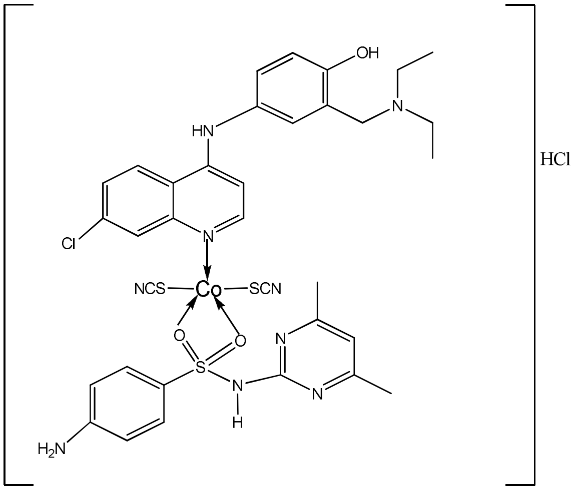

Fig 1. Proposed Structure of [Co (SUF)(AMQ)$(SCN)_2$].C_2H_5OH

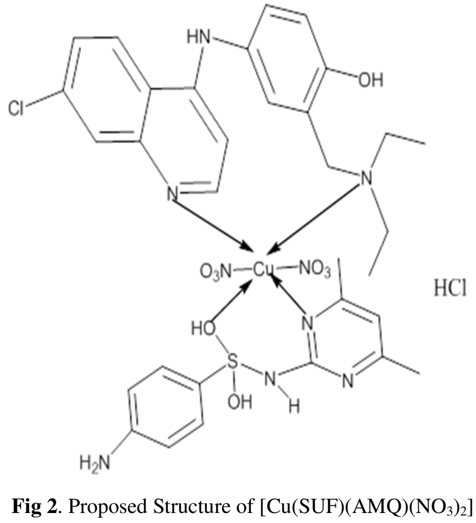

Fig 2. Proposed Structure of [Cu(SUF)(AMQ)$(NO_3)_2$]

Conclusion: The complexes are non-electrolyte in solution and the spectra data of the complexes are consistent with 6-coordinate octahedral complexes. The two ligands behave as a bidentate forming 1:1:1 stoichiometry and octahedral geometry

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