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Preparation and Characterization of Cu (II), Mn(II) and Zn(II)complexes with new sulfamethoxazole Compounds

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Abstract:

Acetophenone sulfamethoxazole and 3-Nitrobenzophenone sulfamethoxazole were prepared from the reaction of sulfamethoxazole with two ketones. The prepared ligands were identified by (C.H.N) analysis and UV-VIS, FT-IR spectroscopic techniques. Metal complexes of the two ligands were prepared in an aqueous alcohol with Zn (II)' Mn (II) and Cu (II) ions with a molar ratio1:1. The proposed general formula for the resulting complexes was $[ML.CL_2.H_2O]H_2O$ .The complexes were characterized by (C.H.N) technique , spectroscopic methods ,conductivity, atomic absorption ,magnetic susceptibility measurements and melting point. According to the results obtained, the suggested geometry is to be octahedral for all the complexes.

Key words: Sulfamethoxazole, Schiff base complexes, Metal complexes, Antibacterial.

Introduction:

Sulfonamides are structural analogs and competitive antagonists of para-amino benzoic acid (PABA). Sulfamethoxazole derivatives are widely used in the medicine and pharmaceutical industry because of their extensive biological effectiveness [1]. Sulfamethoxazole prevents the formation of dihydrofolic acid, a compound which makes the bacteria able to survive. It has been reacted with selected ketons and aldehydes to give Schiff bases [2].Schiff bases play an important role in the coordination chemistry and are used as chelating agents with transition elements [3]. Schiff base metal complexes have a wide interest in clinical, biological and analytical applications [4].They show biological activities including anti bacterial, anti fungal, anti cancer and herbicidal activities, anti-tubercular activities [5]. Moreover, some metal complexes of these ligands have been found to promote rapid healing of burns in humans and animals [6]. The current study investigated the preparation and properties of some metal ion complexes with sulfamethoxazole derivatives.

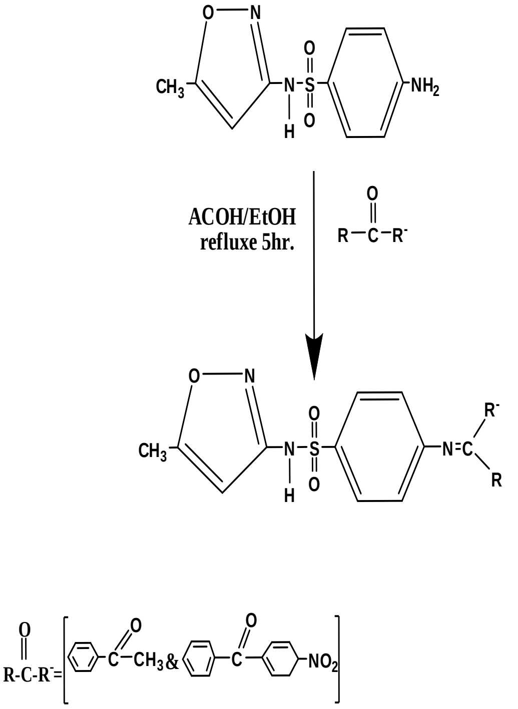
Materials and Methods:

All the chemicals used in this work are of high purity. The electronic spectra were measured on (Shimadzu UV -160 A) Ultra Violet-Visible Spectrophotometer. The infrared spectra were measured using (Shimadzu FTIR-

8600 S) Fourier Transform Infrared, Spectrophotometer (4000-400) cm^{-1} with samples prepared as KBr discs. Metal analysis was determined by using (A.A-680) Shimadzu atomic absorption spectrophotometer. The conductivity measurements were obtained using conduct meter WTW; the complexes were dissolved in DMF, element microanalyses were recorded by microanalysis (C.H.N) in Al-Albaite University in Jordan, the magnetic susceptibility values of the prepared complexes were obtained by using magnetic susceptibility balance Johnosn Matthey. The melting points of the prepared ligands and the complexes were measured by using melting point apparatus Gallenkamp M.F.B-60.

Synthesis of Schiff bases (L1, L2)

Schiff bases L1and L2 were prepared from reaction of sulfamethoxazol (0.01mole) with two different ketones (aceto phenone and4-nitro benzo phenone) (0.01mole in 25 ml absolute ethanol and drops of glacial acetic acide).The mixture was heated under reflux for 5 hrs Precipitates were flittered and recrystallized from ethanol .The synthesis route is shown in Scheme (1).



Scheme 1: Synthesis of Schiff bases (L1, L2).

Preparation of Metal Complexes

An aqueous solution containing 0.17g, 0.136g and 0.197g (1mmole) of $CuCl_2.2H_2O$,$ZnCl_2$ and $MnCl_2.4H_2O$ respectively was added gradually with stirring to ethanolic solution (1mmole) of the ligand (L1). The reaction mixture was heated under reflux for 3 hours, keeping the reaction mixture over night to give solid products and recrystallization from ethanol. The complexes of L2 were prepared by the same method.

Results and Discussion:

The ligands were prepared by condensation reaction between sulfamethoxazol with two different ketones .All prepared complexes were colored, soluble in organic solvent such as EtOH, DMSO and DMF and stable toward air.

(Table1) includes some physical properties and elemental analysis, of prepared ligands and their complexes.

Table (1):- Elemental Analysis and Physical Properties of the Ligands and the Complexes.

Compounds	Color	Yield%	M.P ^{0}C	Elemental microanalysis found. (Calc)%				
				M%	C%	H%	N%	%S
L1	Yellow	85	136	-	52 (51.2)	3.64 (3.80)	10.44 (10.1)	7.58 (6.92)
$[Zn L_1Cl_2(H_2O)]H_2O$	Dark yellow	62	178	10.7 (10.3)	44.63 (44.23)	2.96 (2.88)	8.3 (8.82)	6.25 (6.12)
$[Cu L_1Cl_2(H_2O)]H_2O$	Dark green	50	172	9. 4 (10)	42.57 (43.63)	2.31 (2.84)	8.15 (8.85)	6.8 (6.45)
$[Mn L_1Cl_2(H_2O)]H_2O$	Cream	54	230	7. 1 (7.8)	44.11 (44.23)	3.00 (2.88)	8.00 (8.97)	6.57 (6.00)
L2	Cream	70	170	-	49.86 (49.23)	(4.30) (4.78)	(16) (16.77)	(12.31) (12.27)
$[Zn L_2Cl_2(H_2O)]H_2O$	Dark yellow	78	180	12.23 (12.39)	41.00 (40.95)	3.64 (3.22)	9.27 (9.83)	8.21 (8.15)
$[Cu L_2Cl_2(H_2O)]H_2O$	Green	55.5	172	14 (14.4)	40 (41)	3.76 (3.23)	6.85 (7.99)	7.98 (7.99)
$[Mn L_2Cl_2(H_2O)]H_2O$	Light yellow	57	146	10.09 (10.6)	34.40 (34.21)	3.28 (3.20)	11.3 (11)	8.31 (8.14)

The Infrared Spectral Studies:

FT-IR spectrum of compound (L1) showed absorption bands at 1593 cm^{-1} , 3387 cm^{-1}, 1161-1327 cm^{-1} , 2839-2989 cm^{-1} , 3089 cm^{-1} , 1373cm^{-1} and 1685 cm^{-1} assigned to ν(C=N) in heterocyclic, ν(N-H), ν(SO_2),ν(C-H) aliphatic, ν(C-H) aromatic ,ν(C-NO_2) and ν(C=N) azomethine of the Schiff base respectively as shown in Table (2). FT-IR spectrum of compound (L2) showed characteristic absorption bands at 1597cm^{-1} , 3379cm^{-1} , 1157,1311 cm^{-1}, 3066-3113 cm^{-1}, 2905cm^{-1} and 1620cm^{-1} due to ν(C=N) in heterocyclic, ν(SO_2),ν(C-H)aromatic ,ν(C-H) aliphatic and ν(C=N) azomethine of the Schiff base respectively as shown in Table (2)[7] .

Comparing the IR spectra of the complexes and free ligands, the following differences were observed:

I. A strong band at (3387)cm^{-1} in the ligands assigned to (NH) group was shifted to lower frequency on chelating with metal ion indicating the (NH) group acting as a coordinating site [8] .

II. The shift of two sulfonamide vibrations (symmetric as well as the asymmetric one) toward lower shift number in the spectra of the complexes as compared to the spectra of corresponding ligands (Table2)further support (M-O) bonding [9] .

III. The strong band at 1597and 1593 cm^{-1} assigned to(C=N) in heterocyclic ring exhibit lower shift as support (M-N) bonding.

IV. The metal complexes show abroad band in the region (3466-3475) cm^{-1} and a new band at 829-833 cm^{-1} that assigned to the (O-H) stretching vibration and out of plane bending of water molecules coordinated to the complexes [10].

V. The new bands observed at (416-570) $cm^{-1}$are tentatively assigned to ν (M-N) and (M-O) (Metal- Ligand) [11, 12].

VI. The appearance of a band at (1685, 1620) cm^{-1} in the ligands assigned to ν(C=N) azomethine, this band remains almost at the same position in the complexes and hence suggests that the azomethine nitrogen is not taking part in coordination [7].

Table (2): FT-IR Bands of Ligands and Metal Complexes

Comp.	ν(OH) Water	ν(C=N) cyclic	ν(C=N) azomethine	ν(C-N)	ν (N-H)	ν(SO_2)	ν(M-O)	ν(M-N)
L1	-	1593	1685	1504	3387	1161 1327	-	-
[Zn L_1Cl_2(H_2O)]H_2O	3475	1597	1616	1473	3213	1157 1319	509	447
[Cu L_1Cl_2(H_2O)]H_2O	3474	1593	1620	1473	3387 3259	1134 1323	524	474
[Mn L_1Cl_2(H_2O)]H_2O	3474	1593	1620	1469	3213	1138 1315	570	442
L2	-	1597	1620	1504	3379	1157 1365	-	-
[Zn L_2Cl_2(H_2O)]H_2O	3465	1597	1616	1473	3213	1091 1315	505	474
[Cu L_2Cl_2(H_2O)]H_2O	3464	1597	1616	1400	3303	1114 1319	574	416
[Mn L_2Cl_2(H_2O)]H_2O	3466	1597	1615	1469	3298	1311	543	420

The Electronic Spectral Studies

The free ligand solution display high intensity peaks in the UVregions at 248 and 311 nm, which are assigned to (π→π*) electronic transitions for functional groups, C=N and S=O respectively [13]. The absorption band appeared at (291nm) which can be attributed to (π→π*) transition for the aromatic system [14].

The spectra of copper complexes exhibit a broad band around (600-755nm) described by the $^2Eg \rightarrow ^2T_2g$ electronic transition [15]. These transitions indicated the copper complexes to be distorted octahedral, the magnetic moment values of Cu complexes are (1.85- 1.86) B.M [16-17].

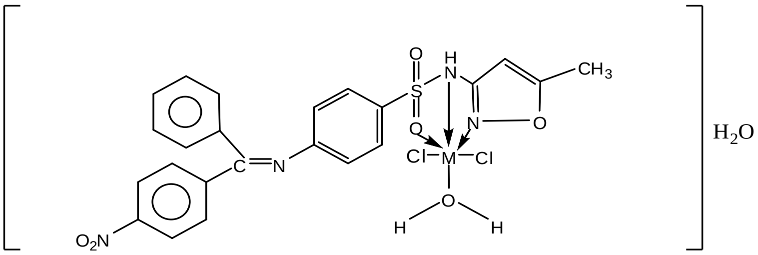
The electronic spectrum of the zinc complexes gave bands at (303, 257 nm) and (408, 285 nm) in [Zn L_1Cl_2 (H_2O)]

H_2O and [Zn L_2Cl_2 (H_2O)] H_2O respectively assigned to charge transfer. The complexes are diamagnetic which are expected for (d^{10}- system) [18].

The electronic spectrum of manganese complexes showed three peaks : the first peak at(257 , 247) nm was attributed to ($^6A_1g\rightarrow{}^4A_1g$),the second peak at(301 , 297)nm was attributed to ($^6A_1g\rightarrow{}^4T_1g$) and the third peak at (302 , 303) nm which was assigned to ($^6A_1g\rightarrow{}^4T_2g$). These transitions indicated these complexes to be octahedral [18]. The molar conductances of the complexes (10^{-3}M) in DMF refer to their non-electrolytic nature. The data are listed in Table 3. The suggested geometry of the complexes can be shown in Figures (1) and(2).

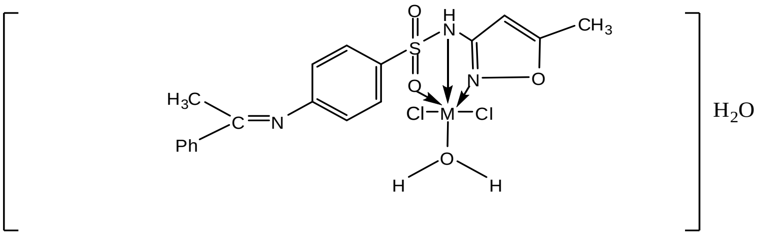
Table 3: Electronic Spectra Data for the Prepared Metal Complexes.

Compounds	(λ nm)	Assignment	*μeff (B.M)*	Molar conductivity	Suggested geometry
L1,L2	248 311 291	$\pi\rightarrow\pi^*$	-	-	-
[Cu L_1Cl_2(H_2O)]H_2O	680 625 640	$^2Eg\rightarrow{}^2T_2g$	1.92	16	O.h
[Cu L_2Cl_2(H_2O)]H_2O	600 737 755	$^2Eg\rightarrow{}^2T_2g$	1.86	12.7	O.h
[Zn L_1Cl_2(H_2O)]H_2O	303 257	C.T	0.00	20	O.h
[Zn L_2Cl_2(H_2O)]H_2O	472 285	C.T	0.00	12.3	O.h
[Mn L_1Cl_2(H_2O)]H_2O	257 301 302	$^6A_1g\rightarrow{}^4A_1g$ $^6A_1g\rightarrow{}^4T_1g$ $^6A_1g\rightarrow{}^4T_2g$	4.92	18.2	O.h
[Mn L_2Cl_2(H_2O)]H_2O	247 297 303	$^6A_1g\rightarrow{}^4A_1g$ $^6A_1g\rightarrow{}^4T_1g$ $^6A_1g\rightarrow{}^4T_2g$	4.88	11	O.h



M= Cu^{+2} , Zn^{+2} , Mn^{+2}

Figure(1) : Complex of 4-Nitro Benzophenone Sulfamethoxazole



M= Cu^{+2} , Zn^{+2} , Mn^{+2}

Figure(2) : Complex of Aceto Benzophenone Sulfamethoxazole

Conclusions:

Tow schiff bases were synthesized from sulfamethoxazole derivatives and characterized .The ligands were treated with metal ions salts to afford corresponding complexes. The complexes showed octahedral geometry around the metal.

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تحضير وتشخيص معقدات الزنك(II) و المنغنيز (II)و النحاس(II) مع ليكاندات جديدة من السلفاميثاكزول

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الخلاصة:

حضر الليكاند 3-نايترو بنزوفينون سلفا ميثاكزول والليكاند بنزوفينون سلفا ميثاكزول من تفاعل السلفاميثاكزول مع كيتونات مختلفة. شخصت الليكاندات المحضرة بواسطة أطياف الأشعة تحت الحمراء وفوق البنفسجية – المرئية والتحليل الدقيق للعناصر(C.H.N) . تمت مفاعلة الليكاندات المحضرة مع ايونات النحاس والزنك والمنغنيز (ثنائية التكافؤ)وشخصت المعقدات المحضرة بوساطة الطرق الفيزيائية المناسبة والتحليل الدقيق للعناصر(C.H.N)، تقنية الامتصاص الذري أللهبي وأطياف الأشعة تحت الحمراء وفوق البنفسجية - المرئية، فضلا عن قياسات التوصيلية الكهربائية والحساسية المغناطيسية ، ومن النتائج التي تم الحصول عليها اقترح الشكل ثماني السطوح للمعقدات المحضرة.

الكلمات المفتاحية: سلفاميثاكزول، معقدات قواعد شيف، المعقدات الفلزية، مضاد للجراثيم.