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Synthesis and characterization of Mn(II) and Cu(II) complexes comprising ketoazosulphapyrimidine

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ABSTRACT

p[p'(2-Pyrimidinyl) sulphonyl benzene]azoacetylacetone(L_1), p[p'(2-pyrimidinyl) sulphonyl benzene]azoethylacetoester(L_2) and their Mn (II) and Cu (II) complexes were prepared and characterized based on elemental analysis, FT-IR and electronic spectral studies, thermal analysis, scanning electronmicroscope (SEM) and X-ray powder diffraction. Thermogravimetric analysis (TGA) was used to follow up the thermal decomposition steps of the ligands and their metal complexes.From the X-ray data, the crystal lattice parameters were computed for two of the complexes. The antimicrobial activity of some synthesized compounds was tested against six fungal and five bacterial species.

KEYWORDS

Ketoazosulphapyrimidine;
Metal complexes;
Thermal studies;
XRD;
Biological activity.

INTRODUCTION

Azo compounds were received much attention and are widely used in many practical applications such as coloring fibers[1], photo electronic applications[2], printing systems[3], optical storage technology[4-5], textile dyes[6-7] as well as in many biological reactions[8-10] and in analytical chemistry[11-12]. Sulfonamides were the first effective chemotherapeutic agents to be employed systematically for the prevention and cure of bacterial infection in human being[13].Sulphonamides are used as drugs for treating cancer, tuberculosis, malaria, diabetes and leprosy[14]. Furthermore, sulphonamide and azosulphonamide derivatives are capable of combination with a large number of metal ions[15,16]. Metal complexes of dyes have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their applications for molecular memory storages, nonlinear optical elements, printing system, etc[17] and therefore, several studies were published on so far[18-26]. In this paper two azosulpha drugs and their Mn(II)and Cu(II) complexes were prepared and characterized in order to throw more light on azosulphonamide derivatives and their metal complexes as they are an important class of compounds.

EXPERIMENTAL

Preparation of the ligands

Preparation of p[p'(2-pyrimidinyl) sulphonyl benzene]azoacetylacetone or the ethylacetoester derivative was done by diazotization of sulphapyrimidine (2.50 g, 10 mmol) in 20 ml hydrochloric acid and 5 ml actetic acid till complete dissolution. Then a cold solution of 5 ml sodium nitrite (0.69 g, 10 mmol) was added

slowly with constant stirring at 0-5°C within two hours to a cold solution of acetylacetone (10 mmol) or ethyl acetoacetate (10 mmol) in 10 ml sodium hydroxide (0.5 g, 15 ml) until the solution became reddish yellow. The solution mixture was then neutralized to pH 6.5-7.5 where a reddish yellow solid precipitated, which was filtered off, washed with water and dried in air. The products were crystallized from ethanol:water (4:1).

Preparation of the complexes

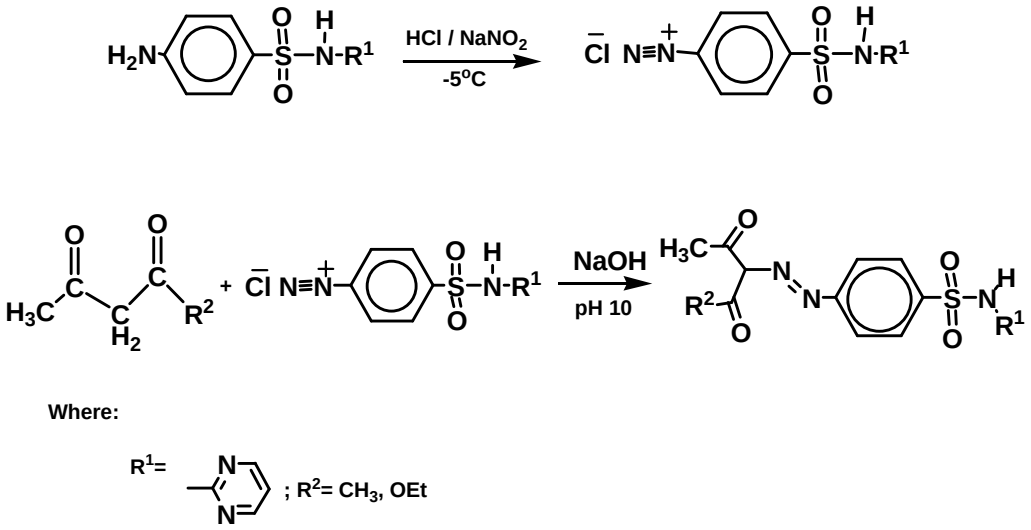
A hot ethanolic solution of an appropriate amount of the two ligands was added to a calculated amount of the respective metal salt (manganese and copper chlorides) dissolved in alcohol with the molar ratio 1:1. After constant stirring for one hour the precipitated complexes were filtered off, washed with ethanol and dried in air.

Physical measurements

Carbon, hydrogen, nitrogen, and sulfur contents of the solid compounds were determined by Elementar Analysen system Gmbh Vario El analyzer. The Fourier transform infrared of all compounds were recorded in the 4000-400 cm^{-1} region with a Shimadzu Spectrophotometer, model (Nicolet 6700), using the KBr disc technique. The electronic absorption spectral measurements in the ultraviolet and visible regions were carried out in DMSO on a UV-2102 PC Shimadzu spectrophotometer using 1 cm matched quartz cell. Magnetic susceptibilies of the compounds were measured at room temperature using a magnetic susceptibility balance of the type MSBAuto. Molar susceptibilities were corrected for diamagnetism of the component atoms by the use of the Pascal's constants. The calibrate used was $Hg[Co(SCN)_4]$. The mass spectra were performed by JOEL JMS 600 Spectrometer at ionizing potential of 70ev using the direct inlet system, at Central Lab, Assiut University. The scanning electron microscope was of the type Joel JSM 5400 LV. The thermal analyses of the compounds were investigated in static air.The TG and DTG thermograms of the compounds were determined by an electrobalance of the type Fisher Scientific XA analytical balance converted to a thermobalance by the addition of a small furnace and a small holder.The temperature was measured using a chromalalumal thermocouple attached to a digital multimeter type soar ME550.The heating rate was adjusted to be 8°C/min. The X-ray diffractometer was a Philips 1700 version with H.T P.W1730/10 4KVA and equipped with a curved graphite single crystal as a monochrometer with an outomatic divergence slit. The whole system was automatically controlled by a microprocessor PW 1710/100. The used anode was CuKα (λ= 1.54180ú).The disc-diffusion method was used to measure the antibacterial activity. The antibacterial activity of the free ligands and their complexes was tested against some strains of bacteria and fungi.

RESULTS AND DISCUSSION

The ligands p[p'(2-pyrimidinyl) sulphonyl



Scheme 1

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benzene]azoacetylacetone, p[p'(2-pyrimidinyl) sulphonyl benzene]azoethylacetoester were prepared by the reaction of acetylacetone or ethylacetoester with azobenzenesulpha pyrimidine, according to scheme1.

The most important infrared spectral bands of the ligands and their complexes are given in TABLE 2. The spectra of the ligands and the complexes display a band in the region 1441-1442 cm^{-1} that can be attributed to ν (N=N) of the azobenzene moiety[27-31]. No appreciable shift was observed in ν (N=N) upon complexation with Mn(II)and Cu(II) but the appearance of ν M-N band at 568-580 cm^{-1} may indicate coordination of Mn(II) and Cu(II) to the azo group. The strong band in the region 1632-1676 cm^{-1} indicates the presence of carbonyl groups of acetylacetone or ethylacetoester. This absorption frequency range for the complexes is shifted to a lower frequency (except for $CuCl_2L_1.2H_2O$) compared to the free ligands (1666-167cm^{-1}) indicating coordination of the two metal ions to the carbonyl groups of the ligands. This is further confirmed by the band observed at 450-490 cm^{-1}assigned to ν M-O. νN-H or ν(OH) H_2O of compounds 2 and 4 is observed in the range 3040-3408 cm^{-1}. No shift was observed in ν NH upon complexation to the ligands which excludes its coordination to the metal ions. Two bands are located in the ranges 1143-1161 $cm^{-1}$and 1331-1384 cm^{-1} assignable to the absorption of $(SO_2)_{sym}$ and $(SO_2)_{asym}$,respectively[32-34]. The absence of observable shift of the -SO_2 stretching frequency in the spectra of the complexes if compared with those of the ligands indicates that there is no interaction between the sulphonyl group and Mn(II) or Cu(II) ions. The ethylacetoester or acetylacetone ligand derivatives as well as their metal complexes exhibit a band in the ranges 760-798 cm^{-1} and 1517-1584 cm^{-1} corresponding to the aromatic ν (C-H) and ν (C=N) of the pyrimidine moiety.

MASS SPECTRA

A mass spectrum was recorded for the ligand L_1 to illucidate its fragmentation pattern and to be as a repre-

TABLE 1 : Physical properties and elemental analysis of the ligands and their complexes

Compound No.	M.F (M.wt)	Color	Decomp mp. °C	Calculated/ (Found)			
				C%	H%	N%	S%
L_1 1	$C_{15}H_{15}N_5O_4S$ (361.31)	Pale brown	210-213	49.86 (49.25)	4.15 (3.72)	19.38 (19.30)	8.87 (8.89)
$L_2.H_2O$ 2	$C_{16}H_{14}N_5O_6S$ (409.58)	Brown	180-182	46.97 (46.74)	4.17 (3.98)	17.09 (17.30)	7.82 (7.65)
$[MnCl_2L_1]$ 3	$C_{15}H_{15}N_5O_4SMnCl_2$ (487.24)	Dark brown	251-354	36.97 (36.88)	3.11 (3.88)	14.37 (14.72)	6.57 (6.13)
$[CuCl_2 L_1]. 2H_2O$ 4	$C_{15}H_{19}N_5O_6SCuCl_2$ (531.75)	Pale brown	218-220	33.94 (32.64)	3.60 (3.65)	13.17 (13.43)	6.02 (6.08)
$[MnCl_2L_2]$ 5	$C_{16}H_{17}N_5O_5SMnCl_2$ (517.41)	Brown	233-235	37.14 (36.15)	3.30 (3.22)	13.58 (12.98)	6.19 (6.87)
$[CuCl_2L_2]$ 6	$C_{16}H_{17}N_5O_5SCuCl_2$ (526.02)	Brown	221-223	36.53 (35.48)	3.25 (3.38)	13.36 (13.91)	6.09 (5.68)

TABLE 2 : IR Spectral data of the complexes (cm^{-1})

Compound	ν(N=N)	ν(C=N)	ν (N-H)/ν(OH)H_2O	ν(C=O)	νSO_2 sym	νSO_2 asym	ν (C-H) (Ar)	ν (M-O)	ν(M-N)
L_1	1441	1582	3040	1676	1154	1334	798	490	575
$L_2.H_2O$	1441	1530	3170 3400	1666	1155	1338	797	465	571
$[MnCl_2L_1]$	1442	1517	3380	1632	1160	1382	797	485	568
$[CuCl_2L_1]. 2H_2O$	1442	1584	3150 3408	1676	1161	1331	785	490	569
$[MnCl_2 L_2]$	1441	1528	3389	1640	1154	1350	797	490	569
$[CuCl_2 L_2]$	1442	1557	3200	1635	1143	1384	760	450	580

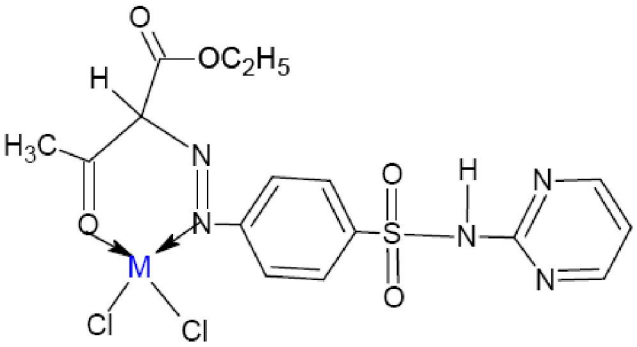
TABLE 3 : Electronic spectral data of the ligands and complexes in DMF solutions (cm^{-1})

Ligand-Complex	ν max (cm^{-1})	Assignment	(B.M)
L_1	19,571	n - π^*	-
	32,679	π - π^*	
$[MnCl_2L_1]$	12,917	d –d	5.75
	21,530	n - π^*	
	34,456	π - π^*	
	38,842	Charge transfer	
$[CuCl_2L_1].2H_2O$	13,801	d –d	2.11
	23,716	n - π^*	
	35,985	π - π^*	
	38,997	Charge transfer	
L_2	21,285	n - π^*	-
	31,243	π - π^*	
$[MnCl_2L_2]$	12,812	d –d	5.77
	23,280	n - π^*	
	33,670	π - π^*	
	38,821	Charge transfer	
$[CuCl_2L_2]$	13,569	d –d	2.11
	22,710	n - π^*	
	33,740	π - π^*	
	39,964	Charge transfer	

sentative for the other compounds. The fragmentation pathway of acetylacetoneazobenzenesulphanoylpyrimidine is characterized by the appearance of a molecular ion peak at m/z 361.03 (0.5%), a fragment at m/z 255.01 (5.2%) for $[M\text{-}C_8H_{12}N_2]^+$ and base peak at m/z 185.02 (100.0%) for $M\text{-}C_6H_{10}O_2N_3S)]^+$ confirming the structure of this compound[40].

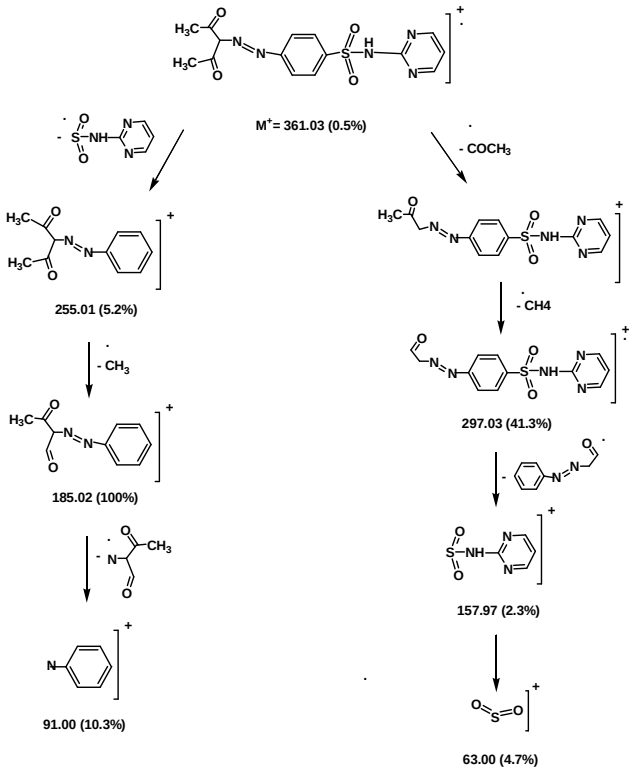
From the above results the structure of the complexes can be deduced. Those of the ethlyacetoester derivative are typical and are illustrated below:

The thermal behavior of six compounds, namely L_1, L_2, $MnCl_2L_1$, $CuCl_2L_1.2H_2O$, $MnCl_2L_2$, $CuCl_2L_2$ was studied in static air. The thermal decomposition of $MnCl_2$ L_1 as a representative compound will be described. Three decomposition steps were observed in



M = Mn(II) or Cu(II).

thermo-gravimetric curve of this comound (Figure 2). The decomposition occurs in the temperature ranges 102-180, 335-520 and 530-650 ºC. The mass loss associated with the first step involves the loss of an acetyl radical (calc.8.8%, found 9.0%). For this step a DTG peak is recorded at 145ºC. The second mass loss (calc.



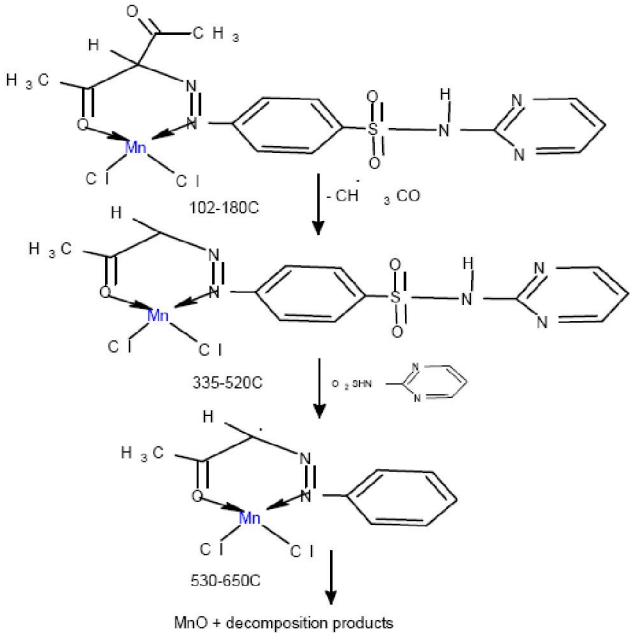


Figure 1

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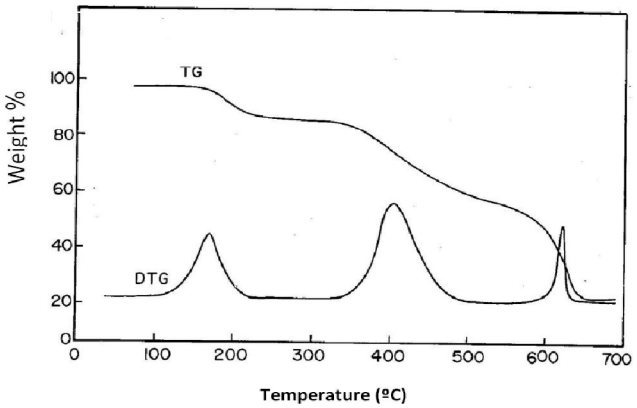

Figure 2 : TG-DTG curves of $[MnCl_2L_1]$

32.4%, found 32.5%) is commensurate with the release of a sulphapyrimidine radical. The third mass loss of 32.0% is manifested on the DTG curve as a peak at 610°C. The end product at 650°C is consistent with the residue MnO (calc.14.6%, found 16.0%).

The thermal decomposition data of the ligands and their complexes are tabulated in TABLE 4.

X.RAY POWDER DIFFRACTION

The crystal lattice parameters were computed with the aid of the computer program TREOR. for complexes 3 and 6. The observed 2θ with relative intensity more than 10% were indexed and were used for evaluation. The program is known to be efficient for indexing low- symmetry crystal systems. The crystal data of the two complexes fit well with the triclinic crystal system (TABLE 5).

Scanning Electron Micrographs (SEM): The scanning electron micrographs of $[CuCl_2L_1].2H_2O$ and $[CuCl_2L_2]$ were recorded. Figure 3 of $[CuCl_2L_1.2H_2O]$ shows a regular spherical shape of the complex particles and the average diameter of the microspheres is 6 μm. For $[CuCl_2L_2]$, Figure 4 reveals that most of the

TABLE 4 : Thermal decomposition data of the ligands and their complexes

Compound	Step	TG/DTG			Mass loss (%)
		T_i/°C	T_m/°C	T_f/°C	
L_1	1st	100	165	253	24.0
	2nd	255	450	610	46.2
$[MnCl_2L_1]$	1st	102	145	180	9.0
	2nd	335	402	520	32.5
	3rd	530	615	650	28.0
$[CuCl_2L_1].2H_2O$	1st	98	148	200	17.8
	2nd	215	255	312	27.2
	3rd	312	397	468	22.5
	4th	490	548	620	13.7
L_2	1st	80	154	200	32.0
	2nd	210	308	418	17.6
	3rd	420	500	580	53.0
$[MnCl_2L_2]$	1st	120	187	255	22.2
	2nd	362	396	446	13.5
	3rd	460	530	625	43.4
$[CuCl_2L_2]$	1st	133	180	216	24.4
	2nd	216	297	368	29.5
	3rd	400	473	586	30.0

TABLE 5 : The crystal data of complexes

Complex	a(Å)	b(Å)	c(Å)	α(d)	β(d)	γ (d)	Volume Unit cell (Å^3)	Crystal system
3	4.32	5.89	15.5	63.3	41.4	71.5	234.3	Triclinic
6	2.79	6.27	8.33	56.8	68.8	86.1	112.5	Triclinic

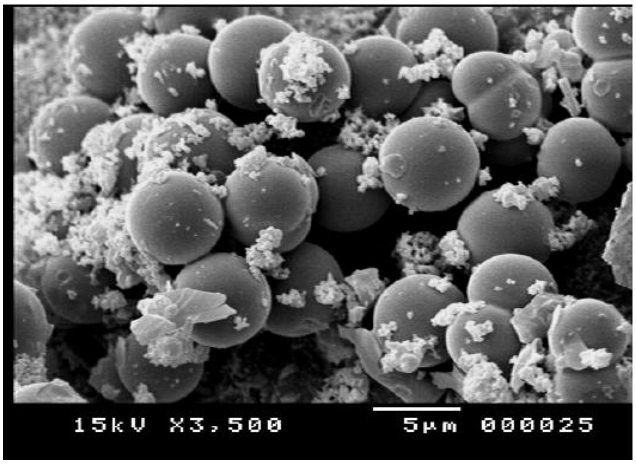

Figure 3 : SEM of $[CuCl_2L_1].2H_2O$

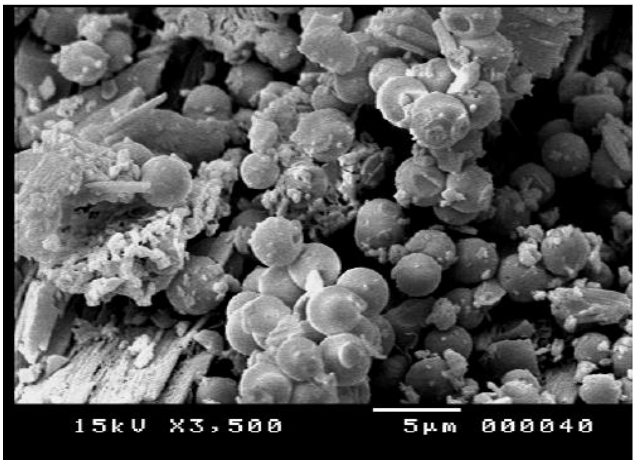

Figure 4 : SEM of $[CuCl_2L_2]$

particles are also spherical and the average diameter is 2.5 µm. The surface of the microspheres of both complexes is clearly smooth which means that there is no preferential direction for the growth of the particles.

Biological activity of selected synthesized compounds was tested against Gram positive and Gram negative bacteria as well as against filamentous fungi (TABLES 7,8). All microbes are potentially pathogenic. The compounds showed varying antimicrobial action depending on the microorganism species and the compound itself. Compounds 1, 2, 3 and 6 proved to be excellent candidates as antibacterial agents being able to inhibit all bacterial species. Regarding to the antifungal action, the fungi species Candida *albicans* causes candidosis in human and animals. Geotrichm *candidum* causes also geotrichosis in human and animals. Trichophyton *rubrum* is usually involved in skin and nail infection, Fusarium *oxysporum* is one of the famous plant pathogens, Aspergillus *Flavus* is a famous allergenic, pathogenic and toxigenic mold and Scopulariopsis *brevicaulis* causes nail infections.

TABLE 7 : Antibacterial activity of the synthesized compounds (inhibition zone in mm)

Compounds	Serratia *marcescens* (-)	Bacillus *cereus* (+)	StaphyoCoCcus *aureus* (+)	Escheichia *coli* (-)	Pseudomonas *aerginosa* (-)
1	16	28	18	28	30
2	20	24	16	19	21
3	23	11	17	15	13
6	16	14	13	18	14

TABLE 8 : Antifungal activity of the synthesized compounds (inhibition zone in mm)

Compds.	Candida *albicans*	Geotrichm *candidum*	Trichophyton *rubrum*	Fusarium *oxysporum*	Aspergillus *flavus*	Scopulariopsis *brevicaulis*
1	11	9	13	17	14	8
2	11	6	15	11	12	14
3	9	0	12	0	21	0
6	0	0	15	0	14	0

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