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Oxalaceto(2-Chloro–6–Fluoro–Benzylidene) and Oxalaceto(2-Chloro-5–Nitrobenzylidene) Hydrazides and Spectroscopic Studies of the Complexes

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Abstract

The synthesis, structure, spectral and biological studies of Cu(II), Mn(II), and Zn(II) complexes of two kind of hydrazides ligand are described. The ligands was derived by the condensation of oxalaetic acid with hydrazine hydrate later substituted with two kind of benzaldehyde. These metal complexes were characterized by elemental analysis, molar conductance, magnetic moment measurements, IR, and spectral data. An octahedral geometry was proposed for all the metal complexes. It is evident from the IR data that in all the complexes, only two part of the ligands is coordinated to the metal ion resulting in binuclear kind of complexes. The ligand coordinates through the nitrogen atoms (C=N) of the azomethine and oxygen atom of the carbonyl compound (C=O) of the hydrazide moiety. The formulations,- [Cu(HL^1)], [Mn(HL^1)], [Zn(HL^1)], and [Cu(HL^2)], [Mn(HL^2)], [Zn(HL^2)], are in accordance with elemental analyses, physical and spectroscopic measurements. The complexes are soluble in organic solvents dimethylsulphoxide (DMSO). Molar conductance values in DMSO indicate the non electrolytic nature of the complexes. The ligands and metal complexes show a good activity against the bacteria; *B. Subtilis, E.coli* and *S.aureus* and fungi *A.niger, A.flavus* and *C.albicans*. The antimicrobial results also indicate that the metal complexes are better antimicrobial agents as compared to the ligands.

INTRODUCTION

The coordination chemistry of transition metals with ligands from the hydrazide family has been of interest due to different bonding modes shown by these ligands with both electron rich and electron poor metals. Hydrazide play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. Hydrazides possessing an azometine -NHN=CH- Proton constitute an important class of compounds for new drug development. Therefore, many researchers have synthesized these compounds as target structures and evaluated their biological activities. Acid hydrazides have frequently been investigated for testing their potentiality as tuberculostats[1]. Hydrazides and their condensation products have displayed diverse range of biological properties such as bactericidal, anti-fungal, anti-convulsant, anti-helmintic, anti-tumor, anti-leprotic, anti-malarial, anti-cancer, anti-depressant, anti-HIV, analgesic-anti-inflammatory, leishmanicidal, vasodilator activities.

The development of the field of bioinorganic chemistry has increased interest in hydrazide complexes, since it has been recognized that many of these complexes may serve as models for biologically important species[1,2]. Structural studies have shown that hydrazides exhibit different types of bonding depending on the nature of the metal ion and the reaction condition. The interest in such complexes continues increasing due to the possibility of their use as models to explain some intricate reaction in biological systems.

Experimental

Melting points were taken in open glass capillaries and are uncorrected. All the used chemicals and solvents were of Anal R grade. All the reagents and metal salts used for the preparation of the ligands were obtained from Sigma Aldrich. Elemental analyses were performed using EDTA titration. FT-IR spectra were recorded in KBr medium on a Perkin Elmer RX1 spectrophotometer in wave number 4000-400 cm^{-1}. Electronic spectra (in DMSO) were recorded using perkin Elmer Lambda-2B-spectrophotometer. Molar conductance measurements were conducted using 10^{-3} M solutions of the complexes in DMSO on Elico-CM 82 Conductivity Bridge at room temperature. The magnetic susceptibilities measurement were taken on a Gouy balance at room temperature using mercuric tetrathiocyanatocobaltate(II) as the calibrant.

Preparation of the ligands

The ligands were prepared according to literature.

The ligands (HL^1 and HL^2) were prepared by mixtures of oxalacetic acid (16.8g, 0.14 moles) and hydrazine hydrate (16.8g, 0.14 moles) in 100 ml ethanol for 6 hours. The isolated compounds were filtered off as white crystals, washed with ether, recrystallised from absolute ethanol and finally dried. (yield % = 76).

Equimolar mixture of (oxalacetohydrazide) (0.27g, 0.001 mol) was refluxed with the derivative aldehyde i.e (2-chloro-6-fluorobenzaldehyde) (0.27g, 0.001 mol) and (2-chloro-5-nitrobenzaldehyde) (0.27g, 0.001 mol) in 50 ml ethanol for 4 hours. The precipitate was filtered, washed with cold EtOH several times and crystallised from acetone-water and dried. (yield% = 86). (scheme-1).

Preparation of the Cu(II), Mn(II) and Zn(II) complexes

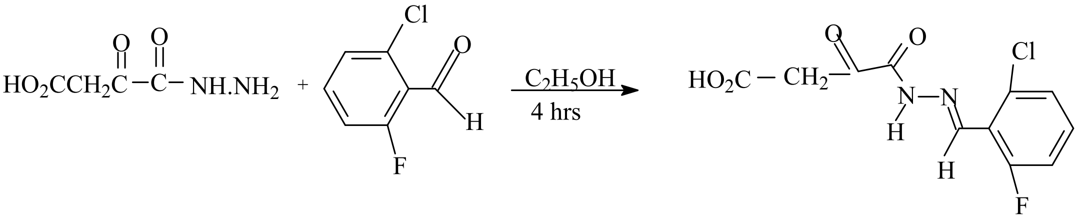
A sample of ligands (HL^1 and HL^2) (0.27g, 0.001 mol) each was dissolved in absolute ethanol (50 ml). A solution of nitrate salts of metal [$Cu(NO_3)_2$ (0.05g, 0.002 mol), $Mn(NO_3)_2$ (0.06g, 0.002 mol), $Zn(NO_3)_2$ (0.04g, 0.002 mol)] in 50 ml of absolute ethanol was added drop wise to the ligands solution with continuous stirring. The complex started to form immediately upon addition of the metal salt solution. The precipitated complex was filtered off, washed with H_2O, cold EtOH several times and dried. (scheme-1)

Antibacterial activities:

Antibacterial activity of hydrazide/hydrazone (ligands) and its metal complexes were studied against gram-positive bacteria (*Bacillus subtilis and Staphylococcus aureus*) and gram-negative bacteria (*E.coli)* at a concentration of 50µg/mL by nutrient agar disk method. Dimethly sulfuroxide (DMSO) system was used as control in this method and the area of inhibition of zone measured in mm. The antifungal activities of the compounds were also tested by the well diffusion method against the fungi: *A. Niger, A. flavus* and *C. albicans,* on potato dextrose agar as the medium and Griseofulvin as control. The stock solution was prepared by dissolving the compound in DMSO. In a typical procedure, as well was made on a agar medium inoculated with the fungi. The well was filled with the test solution using a micro-pipette and the plate was incubated 72 hours at 30 ^0C. During this period, the test solution diffused and growth of the inoculated fungi was affected. The inhibition zone was developed, at which the concentration was noted [5].

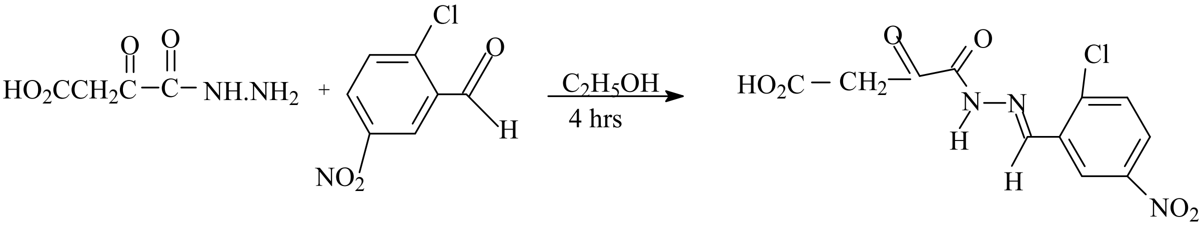
Results and Discussion

The analytical data along with some physical properties of the complexes are summarized in table 1. The ligands (HL^1 and HL^2), on interaction with Cu(II), Mn(II) and Zn(II) nitrates, yields complexes corresponding to the general formula $[M(HL^1)_2(NO_3)_2].H_2O$ and $[M(HL^2)_2(NO_3)_2].H_2O$. The analytical data show that the metal to ligand ratio is 1:2. They are soluble in dimethylsulfuroxide (DMSO) and insoluble in H_2O, n-hexane, benzene etc. The low molar conductance values of the complexes reveal their non-electrolytic nature of the metal (II) salts. The preparation of ligands (HL^1 and HL^2), and the metal (II) complexes were represented by the following equations below:



oxalaceto (2-chloro-6-fluoro-benzylidene)hydrazide

[HL^1]



oxalaceto (2-choloro-5-nitro-benzylidene) hydrazide

[HL^2]

$$M(NO_3)_2 + [HL^1] \xrightarrow[H_2O]{C_2H_5OH} [M(HL^1)_2(NO_3)_2].H_2O + H_2O$$

$$M(NO_3)_2 + [HL^2] \xrightarrow[H_2O]{C_2H_5OH} [M(HL^2)_2(NO_3)_2].H_2O + H_2O$$

Where M = Cu(II), Mn(II) and Zn(II) and $HL^1 = C_{11}H_8N_2O_4FCl$ and $HL^2 = C_{11}H_8N_3O_7Cl$

Scheme-1: preparation of ligands and complexes

Table 1: Elemental analysis of the Ligands and metal complexes

Conpounds (Empirical Formula)	Colour	Formula weight	% yield	Anal. Found (Cal.) % C	H	N	M	^m mhocm^2 mol^{-1}
[HL^1]	Off white	287	76	46.09	2.81	9.78		
				(46.05)	(3.91)	(9.78)	-	-
$C_{11}H_8N_4O_{10}FClCu$	Dark green	474	81	27.84	1.70	11.82	13.40	
				(27.83)	(1.65)	(11.79)	(13.42)	14.13
$C_{11}H_8N_4O_{10}FClMn$	Brown	465	56	28.37	1.73	12.03	11.80	
				(28.40)	(1.71)	(12.03)	(11.79)	12.14
$C_{11}H_8N_4O_{10}FClZn$	Black	476	66	27.75	1.69	11.77	13.73	
				(27.70)	(1.70)	(11.70)	(13.75)	10.11
[HL^2]	Off white	329	86	40.08	2.45	12.75		
				(40.10)	(2.35)	(12.80)	-	-
$C_{11}H_8N_5O_{13}ClCu$	Green	517	77	25.54	1.56	13.54	12.29	
				(25.05)	(1.55)	(12.78)	(12.29)	11.00
$C_{11}H_8N_5O_{13}ClMn$	Dark brown	508	55	25.97	1.59	13.77	10.80	
				(25.95)	(1.67)	(12.99)	(10.85)	11.00
$C_{11}H_8N_5O_{13}ClZn$	Brown	519	82	25.45	1.55	13.49	12.59	
				(25.61)	(1.60)	(13.47)	(12.65)	10.00

The infrared spectra of the complexes taken in the region 400-4000 cm^{-1} were compared with those of the free ligands. There are some significant changes between the metal (II) complexes and their free ligands for chelation as expected [6]. The main stretching frequencies of the IR spectra of the ligands (HL^1) and (HL^2) and their complexes are tabulated in Table-2. An exhaustive comparison of the IR spectra of the ligands and complexes gave information about the mode of bonding of the ligands in metal complexes.

Table 2. IR spectral Bands oof ligands and its metal complexes

Compound	υ(C=O)	υ(C=N)	υ(N-N)	υ(M-N)	υ(M-O)	υ(OH)
$C_{11}H_8N_2O_4FCl$	1628	1533	1080	-	-	-
$C_{11}H_8N_4O_{10}FClCU$	1620	1525	1085	400	530	3300
$C_{11}H_8N_4O_{10}FClMn$	1625	1520	1084	450	508	3320
$C_{11}H_8N_4O_{10}FClZn$	1622	1522	1081	461	525	3400
$C_{11}H_8N_3O_7Cl$	1647	1567	10883	-	-	-
$C_{11}H_8N_5O_{13}ClCu$	1640	1555	1088	408	520	3335
$C_{11}H_8N_5O_{13}ClMn$	1645	1550	1086	425	555	3310
$C_{11}H_8N_5O_{13}ClZn$	1630	1550	1085	455	510	3325

The ligands showed a weak broad band around 2890 and 3068 cm^{-1}, but the IR spectra of metal (II) complexes exhibited intense broad band near 3300-3400 cm^{-1} due to υ(OH) of coordinated water molecule [7]. In the IR spectra of the ligands an intense band appearing around 1628 and 1647 cm^{-1} is attributed to υ(C=O) (carbonyl groups). This band is shifted to lower wave number in the spectra of all the complexes indicating coordination through oxygen of υ(C=O) group. The medium intensity band appearing around 1533 and 1567 cm^{-1} in the ligands are assigned to υ (C=N) (zomethine). This is also shifted to lower frequency in all metal complexes, suggesting that this group takes part in coordination. The coordination of nitrogen to the metal atom would be expected to reduce electron density on the azomethine link and thus cause a shift in the C=N band. The small shift to higher frequency of the band due to υ(N-N) can be taken as additional evidence of the participation of the azomethine group in bonding. This result is confirmed by the presence of a new band at 508-555 cm^{-1} and 400-461 cm^{-1} ; these bands can be assigned to υ(M-O) and υ(M-N) vibrations, respectively [8].

Electronic spectra

The absorption bands for the complexes will help to give an idea of their structure [6,7]. The electronic spectrum of

Cu(II) complexes shows two broad bands around 15,377 cm^{-1} and 22,726 cm^{-1}. The first bands may be due to $^2T_{2g} \rightarrow {}^2E_g$ transition, while the second may be due to charge transfer[9]. The electronic spectra of Mn(II) complexes show the absorption bands in the range 16970–19540, 22280–24390 and 26109–27624 cm^{-1}. These absorption bands may be assigned to the $^6A_{1g} \rightarrow {}^4A_{1g}$ (4G), $^6A_{1g} \rightarrow {}^4A_{2g}$ (4G), and $^6A_{1g} \rightarrow {}^4Eg$, $^4A_{1g}$ (4G) transitions, respectively. These bands suggest that the complexes possess an octahedral geometry[10]. The Zn(II) complex has not shown any d–d absorptions the complexes exhibit two kind of electronic spectrum at 29,145 and 28,225 cm^{-1}, assigned to the charge transfer transition[9,10].

Magnetic Measurements

The magnetic moment values are useful in the evaluation of results provided by the other techniques of the structural investigation [11]. The magnetic moment data are presented in table-3. The magnetic moment of the Cu(II) complex is (1.80 and 1.85 B.M.) which is very close to the spin-only value (1.73 B.M.)[12]. The Mn(II) complex show magnetic moments of (5.25 and 5.52 B.M). at room temperature corresponding to five unpaired electrons which suggest octahedral geometry [11,12]. Since Zn(II) is diamagnetic in nature.

Table 3: Electronic Spectral Bands and Magnetic Moment Values of Complexes

Compounds	M.pt °C	Magnetic moment B.M	Absorption Maxima (cm^{-1})	Transition Assignment
$C_{11}H_8N_4O_{10}FClCu$	220	1.80	15,377 22,726	$^2T_{2g} \rightarrow {}^2E_g$ Charge transfer
$C_{11}H_8N_4O_{10}FClMn$	210	5.25	16970–19540 22280–24390 26109–27624	$^6A_{1g} \rightarrow {}^4A_{1g}$ (4G) $^6A_{1g} \rightarrow {}^4A_{2g}$ (4G), $^6A_{1g} \rightarrow {}^4E_g$ (4G)
$C_{11}H_8N_4O_{10}FClZn$	179	Diamagnetic	29,145	Charge transfer
$C_{11}H_8N_5O_{13}ClCu$	220	1.85	15,377 22,726	$^2T_{2g} \rightarrow {}^2E_g$ Charge transfer
$C_{11}H_8N_5O_{13}ClMn$	201	5.52	16,471, 17,688 23,160	$^6A_{1g} \rightarrow {}^4T_{1g}$(4G), $^6A_{1g} \rightarrow {}^4T_{2g}$(4G) $^6A_{1g} \rightarrow {}^4A_{1g}$ (4G)
$C_{11}H_8N_5O_{13}ClZn$	199	Diamagnetic	28,225	Charge transfer

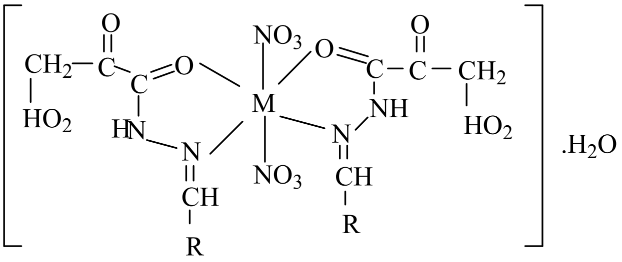
Antimicrobial activities: The bactericidal and fungicidal investigation data of the compounds are summarized in **Table 4**. The results of the investigations account for the antipathogenic behaviour of the compounds and this efficacy is positively modified on complexation. Overtone's Concept and Chelation Theory explain well this drug action

Table 4. In-vitro antibacterial activity of compounds and their inhibition zone (%).

	Antibacterial activity			**Antifungal activity**		
Compounds	*B. subtilis*	*E. coli*	*S. aureus*	*A. niger*	*A. flavus*	*C. albicans*
$C_{11}H_8N_2O_4FCl$	12	18	18	15	10	12
$C_{11}H_8N_4O_{10}FClCu$	20	30	20	25	22	15
$C_{11}H_8N_4O_{10}FClMn$	25	28	33	22	28	15
$C_{11}H_8N_4O_{10}FClZn$	23	30	27	21	20	18
$C_{11}H_8N_3O_7Cl$	15	12	15	20	12	12
$C_{11}H_8N_5O_{13}ClCu$	27	20	22	28	23	20
$C_{11}H_8N_5O_{13}ClMn$	25	18	20	18	18	18
$C_{11}H_8N_5O_{13}ClZn$	20	20	18	22	20	20
Streptomycin	30	38	36	-	-	-
Griseofulvin	-	-	-	30	32	25

Conclusion

From the elemental analysis, molar conductivity, UV-Visible, magnetic, and electronic spectral data it was possible to determine the type of coordination of the ligands in their metal complexes. In all the complexes, only one part of the ligand is coordinated to the metal ion resulting as bidentate complex. The ligand coordinates through the nitrogen atoms (C=N) of the azomethine moiety and oxygen atom of the carbonyl group (C=O). (FIGURE-1). The preliminary studies showed their good inhibitory properties. In general Cu(II), Mn(II) and Zn(II) complexes are more active than their parent ligand and hence may serve as vehicles for activation of the ligand as principle cytotoxic species.



Structure of complex: $[M(HL^1)_2(NO_3)_2]$ H_2O and $[M(HL^2)_2(NO_3)_2]$ H_2O

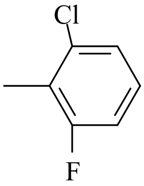
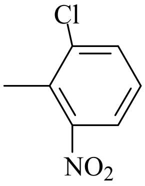
Where M = Cu(II), Mn(II) Zn(II)and R=  for $[HL^1]$ and  for $[HL^2]$

FIGURE 1

Acknowledgment

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