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Synthesis and spectral studies of β-diketone metal complexes

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ABSTRACT

New transition metal complexes having higher oxidation state were prepared from β-iketone. The β-diketone (1-(5-chloro-2-hydroxyphenyl)-3-(3,4-dimethoxyphenyl) propane-1,3-dione) was obtained by template reaction of 2-hydroxy acetophenone with 3, 4 dimethoxy benzoic acid. The compounds were isolated as stable solid complexes with 1:2 metal to ligand ratio and characterized by elemental analysis, conductivity, magnetic measurements, electronic and IR spectroscopy. The XRD recorded from powder forms of all samples shows a definite crystalline system. The obtained lattice parameter values were found to be in good agreement with the proposed structures. All the metal complexes are screened for antibacterial and antifungal activities.

KEYWORDS

β-diketone;
XRD;
Antibacterial activity;
Antifungal activity;
Metal complexes.

INTRODUCTION

One of the pillars of molecular magnetism is the synthesis of novel materials aimed at discovering new properties[1]. In recent years the formation of inorganic-organic hybrid solids formed by the coordination of multidentate ligands to metal ions is a growing field of scientific interest. These coordination compounds have many interesting properties based on their high degree of order. Multidentate rigid ligands can be used to form porous crystals[2,3]. From few years, some of us have devoted efforts to designing and synthesizing a class of ligands displaying linear arrays of oxygen donors based on the adjacent disposition of phenol and 1,3 diketone groups, with the aim of favoring the formation of chains of closely spaced transition metals[1,4]. As well as the d-transition metal- β-diketone compounds were used extensively as starting materials in the early days of metallocene chemistry[5]. Currently complexes containing the pentanedionato ligand have been the focus of much investigations as electroluminescent materials[6-7], presumably due to their ease of preparation, high stability and high volatility in comparison to other chelate complexes[8-9]. The pentanedionato ligand possesses a rather complicated coordination behavior towards redox- active transition metal ions because it can exist in various protonated forms[10]. Studies on the structures of β-diketone metal complexes and their characterization are being of more and more interest to chemists and biochemists[11,12]. Hence we present new series of β-diketone metal complexes with six different metals.

EXPERIMENTAL

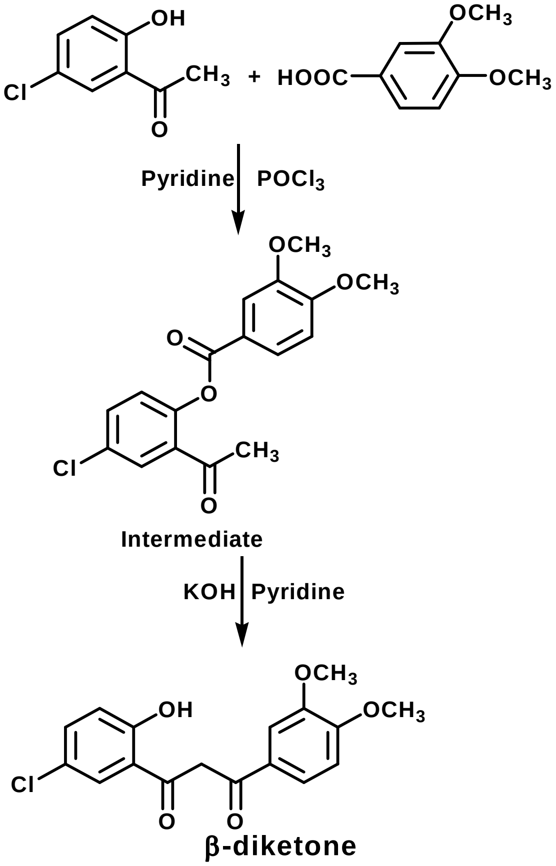
Apparatus and reagents

All the solvents were of analytical grade and were used after distillation. Manganese (III) acetate dihydrate, zirconium acetate and 2-hydroxy acetophenone were synthesized according to published procedures[13,14,15]. Ferric chloride (anhydrous), titanium trichloride (anhydrous), uranyl acetate (dehydrate) (S.D. fine chemicals), vanadyl sulphate (Loba chemie) were used for synthesis. Other reagents and solvents were of AR grade.

Micro analytical data of the ligand and complexes were performed at RSIC, Central Drug Research Institute (CDRI), Lucknow (India). Melting points were determined in open capillaries apparatus. The reactions were monitored by TLC. IR spectra were recorded on a matrix of KBr with FTIR-4100 (Jasco, Japan) spectrometer. ^{1}H NMR spectra were recorded on Varian NMR spectrometer, Model Mercury Plus (200 MHz) and the chemical shifts are given in ppm relative to TMS as an internal standard. ^{13}C NMR spectra were recorded on Varian NMR spectrometer, Model Mercury Plus (50MHz) in $CDCl_3$ and the chemical shifts are given in ppm relative to TMS as an internal standard. The magnetic measurements were carried out by Gouy method at room temperature using $Hg[Co(SCN)_4]$ as the calibrant. The electronic spectra were recorded in DMF solution on a 530 (Jasco, Japan) spectrophotometer in the range between 200-1100nm. The molar conductance of the complexes at 10^{-3}M dilution in DMF were determined using Elico CM 180 digital conductivity meter with a conductivity cell of cell constant 1.00 at room temperature. Powder XRD spectra were recorded on BRUCKER AXS $D_{8.}$

Synthesis of ligand

Esterification of 2-hydroxy acetophenone (1mmol) was done with stirring with 3,4-dimethoxy benzoic acid (1 mmol) in pyridine for 4-5 h using $POCl_3$ as a catalyst and kept for overnight. The crimson coloured product was obtained as a starting material for further reaction. The obtained ester (1mmol) dissolved in pyridine and powdered KOH (2mmol) was added and stirred about 3-4h. The mixture was poured in ice cold water and concentrated HCl. Finally yellow coloured product was obtained which was recrystallized from distilled ethanol. (Yield 74%) m.p. 128°C. The schematic representation is given in Scheme 1.



Scheme 1 : Synthesis of 1-(5-chloro-2-hydroxyphenyl)-3-(3,4-dimethoxyphenyl)propane-1,3-dione

Synthesis of Fe (III), Mn (III), Ti (III), VO(VI) and UO_2 (VI) metal complexes

A methanolic solution of appropriate metal salt (10mmol) was added in ethanolic solution of ligand (25-30mL) and heated over a boiling water bath. A pinch of sodium acetate (2g) was added in reaction mixture to avoid the oxidation and then refluxed with stirring for 5 h using a $CaCl_2$ guard tube. The colored crystalline product was formed, which was separated by filtration, washed with aqueous ethanolic solution and finally with petroleum ether and recrystallized from DMF. The product was dried over fused calcium chloride in desiccators. Yield (60%).

Synthesis of Zr(IV) complex

Zr(IV) metal complex was prepared by following recently published literature method[16]. Zirconyl oxychloride octahydrate (1.64 g, 2mmol) was dissolved in methanol (15mL) and anhydrous sodium acetate (0.32g, 4mmol in 15mL methanol) was added in it. The mixture was then stirred for 5 min. The separated sodium chloride was filtered off and discarded. To the remaining solution, containing oxozirconium (IV) diacetate, the ethanolic ligand solution (2mmol) was added. The mixture was refluxed for 6h. The lime-colored product obtained was filtered and washed 2-3 times with methanol followed by water then petroleum ether, and dried at room temperature. Yield 60-70%.

Antimicrobial screening

The *in vitro* biological screening effects of the investigated compounds were tested against gram positive bacteria, *i.e. S. aureus, S. typhi, B. subtilis* and gram negative bacteria, *i.e. E. coli* and *P. aeruginosa* by paper disc plate method[16] using agar as the GN nutrient medium and streptomycin as standard. The concentration of the compound used for testing was 1μg/0.02ml in DMF.

In a typical procedure, the 10mm diameter Whatmann no.1 paper discs were soaked in different solutions of the compounds, dried, and then placed in petri plates previously seeded with the test organism and the plate was incubated at 37°C for 24h. During this period, the test solution diffused and the growth of microorganism was affected. The antibacterial activity was estimated on the basis of the size of the inhibition zone around the discs.

Fungicidal activity of the ligands and corresponding metal complexes, their effect on the growth of fungi was studied. All the fungi belong to family *Aspergillus. F*ive different species of Aspergillus fungi *i.e. A. flavus, A. niger, A. ustus, A. fumigatus and A. glaucus* were studied for this purpose. The ligand and their corresponding metal chelates in DMF *in vitro* for their fungicidal activity in glucose nitrate medium were screened by mycelia dry weight method[17]. Two different concentration levels of 125ppm and 250ppm were used.

RESULT AND DISCUSSION

All the metal complexes are colored solids, air stable and soluble in DMF and DMSO. The elemental analysis shows 1:2 (metal**:**ligand) stoicheometry for all the complexes. The micro analytical data, molar conductance and other data of the ligand and the complexes are given in TABLE 1. The presence of chlorine in Fe(III) complex was confirmed by Volhard's test. The metal contents in complexes were analysed by gravimetric analysis by the standard methods[18]. All the complexes show low conductance which indicates their non-electrolytic nature. The Ti(III), Mn(III), Fe(III), and VO(IV) complexes exhibit paramagnetic nature whereas the Zr(IV), UO_2(VI) are diamagnetic in nature.

NMR spectra

In ^{1}H-NMR spectra (300 MHz, $CDCl_3$, δppm) of the ligand shows signals at 3.95, 3.96(6H, t, C6-OCH_3), 6.4-7.65 (6H, m, phenyl ring), 12.04 (1H. s, phenolic -OH), and 15.81 (1H, s, enolic -OH).

TABLE 1 : Physical characterization, analytical and molar conductance data of the compound

Comp./Complexes	Color	Formula Weight (cald.)	M.P./ Decomp. (°C)	Elemental Analysis%Found (cald.)				Yield (%)	λM($\Omega^{-1}cm^2$ $mol^{-1}\times10^{-2}$)
				M	C	H	O		
$(LH)_1$	Yellow	334.76	130	----	67.99	5.37	26.44	74	----
$UO_2[(LH)_2]$	Orange	986.69	299	24.12 (24.35)	46.26 (46.57)	4.60 (4.72)	17.84 (17.82)	60	49
$Fe[(LH)_2(H_2O)(Cl)]$	Brown	762.68	312	7.32 (7.89)	55.14 (55.72)	5.16 (5.32)	23.08 (23.12)	60	50
$Ti[(LH)_2\ (H_2O)(Cl)]$	Yellow	789.02	280	6.06 (6.36)	53.22 (53.2)	4.98 (5.23)	22.28 (22.30)	60	32
$Zr[(LH)_2(H_2O)_2]$	Yellow	861.89	309	10.58 (10.92)	51.56 (51.62)	5.50 (5.60)	24.13 (24.20)	70	61
$Mn[(LH)_2(H_2O)(OAc)]$	Brown	913.17 (911.21)	314	6.02 (6.09)	55.24 (55.62)	6.07 (6.10)	21.02 (21.12)	60	49
$VO[(LH)_2]$	green	799.60	265	6.37 (6.57)	57.08 (57.67)	5.67 (5.34)	22.01 (22.15)	60	54

In the ^{13}C-NMR spectra (50 MHz, $CDCl_3$, δppm) of the ligand, shows peaks at 55.96, 90.99, 109.35, 110.07, 110.67, 120.26, 121.15, 127.43, 130.11, 135.13.

IR spectra

The free ligand shows a broad band at 1770cm^{-1} indicating that the ligand exhibits the keto form in the solid state. The(C=O) band is shifted to lower frequency by

32-50cm^{-1} in the metal complexes whereas (C-O) band is present at 1516 cm^{-1} in the ligand which is shifted to higher frequency in metal complexes suggesting the participation of C=O (acetyl carbonyl) in coordination[19,20].

The two broad bands in the region 2800-3500cm^{-1} were present in the spectra of the Fe(III), Mn(III), Ti(III) and Zr(IV) metal complexes. One band is due to water molecules present in the metal complexes in the form of lattice water or coordinated water[21] and other band suggests the existence of the compounds predominantly in the intramolecular hydrogen bonded enolic form. This broad band remained almost unaffected in the IR spectra of the complexes, indicating that the enolic OH is not replaced during complex formation[22].

The IR spectrum of the Mn(III) complex displays two additional bands at 1612 and 1435cm^{-1} due to asymmetric and symmetric stretching modes of the acetate group. The separation ($\Delta\nu$~175) of acetate stretching vibrations and their relative intensities agrees well with the acetate group coordinating in its monodentate nature. In the spectra of VO(IV) and Zr(IV) complexes, the additional bands observed at 963cm^{-1}, 1140cm^{-1} and 952cm^{-1} are due to the ν(V=O), ν(Zr-OH) and ν(U=O) modes respectively[23]. In the far infrared region of all complexes, the bands observed in the region 407-556cm^{-1} can be assigned to M-O. All the values are given in TABLE 2. Hence, the ligand coordinates with the metal ions as mono deprotonated bidentate and the coordination occurs via both acetyl oxygen of β-diketone moiety.

UV-vis spectra

The electronic absorption spectra of the ligand and it's UO_2(VI), Mn(III), Ti(III), Fe(III), VO(IV) and Zr(IV) complexes were recorded at room temperature using DMF as the solvent and obtained values are given in TABLE 3. The electronic spectra of the free ligand show a broad band at 25,706cm^{-1} which is assigned to (C=O) transitions[24].

TABLE 2 : Characteristic IR frequencies of the ligand and its metal complexes (cm^{-1})

Compound	ν(C=O)	ν(C-O)	ν(M-O)	νOH	ν(OH)Coord. H_2Omolecule
HL	1770.33	1568.12	---	3050.34	---
$Fe[(LH)_2(H_2O)(Cl)]$	1734.66	1595.81	426.19	3652.52	2938.98
$Mn[(LH)_2(H_2O)(OAc)]$	1762.62	1600.03	524.54	3703.52	3058.33
$Ti[(LH)_2 (H_2O)(Cl)]$	1742.35	1594.12	4887.26	3612.45	2942.52
$VO[(LH)_2]$	1719.23	1509.99	963.27	3084.58	----
$UO_2[(LH)_{2]}$	1756.83	1593.88	952.66	3165.55	----
$Zr[(LH)_2(H_2O)_2]$	1736.58	1502.28	1140.69	3655.41	2940.51

The spectra of the Ti(III) complex exhibits a broad band at 20,536cm^{-1} due to the $^5T_{2g}\rightarrow{}^5E_g$ transition in the ligand. The broad and double-hump nature of the spectrum indicates John-Taller distortion and suggests octahedral geometry[25]. For VO(IV) complex, we observed bands at 26178cm^{-1}, 17152cm^{-1} and 13537cm^{-1} assigned to $^2B_2\rightarrow{}^2E$, $^2B_2\rightarrow{}^2B_1$ and $^2B_2\rightarrow{}^2A_1$ transitions, respectively which confirm square pyramidal geometry. The Mn (III) complex shows three intense bands at 13513cm^{-1}, 16181cm^{-1}, 22100cm^{-1}due to the transitions $^5B_1\rightarrow{}^5B_2$, $^5B_1\rightarrow{}^5A_1$, $^5B_1\rightarrow{}^5E$ and 26178cm^{-1} assigned as ligand metal charge transfer (LMCT) which confirms square pyramidal geometry. The Fe(III) complex shows absorption in the region 16181cm^{-1}, 18,248cm^{-1} and 25906cm^{-1} corresponding to $^6A_1g(S)\rightarrow{}^4T_1g(G)$, $^6A_1g(S)\rightarrow{}^4T_2g(G)$, $^6A_1g(S)\rightarrow{}^4E_g$ transitions supporting high spin octahedral geometry. The UO_2(VI) shows intense band at 26881 cm^{-1} indicates LMCT transition which is not sufficient in deciding the geometry of metal complex[26]. The Zr(IV) metal complex shows bands at 27356cm^{-1} and 31560cm^{-1} both assigned to charge transfer band[27].

TABLE 3 : Magnetic and electronic absorption spectra of ligand and its metal complexes

Ligand/complexes	Magnetic moment (B.M.)	Frequency in cm^{-1}	Band assignment	Geometry
HL	---	25906	^{a}INCT	----
$Fe[(LH)_2(H_2O)(Cl)]$	6.25	16181 25635	$^6A_1g(S)\rightarrow{}^4T_1g(G)$ $^6A_1g\ S)\rightarrow{}^4T_2g(G)$	octahedral
$Mn[(LH)_2(H_2O)(OAc)]$	4.77	13513 17152 22100 26178	$^5B_1\rightarrow{}^5B_2$ $^5B_1\rightarrow{}^5A_1$ $^5B_1\rightarrow{}^5E$ LMCT	Square-pyramidal
$Ti[(LH)_2 (H_2O)(Cl)]$	1.74	20536	$^2T_{2g}\rightarrow{}^2E_g$	Octahedral
$VO[(LH)_2]$	1.76	13537 17530 29411	$^2B_2\rightarrow{}^2E$ $^2B_2\rightarrow{}^2B_1$ $^2B_2\rightarrow{}^2A_1$	Square Pyramidal
$UO_2[(LH)_2]$	Dia.	26881	^{b}LMCT	------
$Zr[(LH)_2(H_2O)_2]$	Dia.	27356 31560	^{b}LMCT	octahedral

^{a}INCT : Intra- ligand charge transfer, ^{b}LMCT : Metal to ligand charge transfer, Dia.: Diamagnetic.

Magnetic moments of the complexes were measured at room temperature. From the magnetic susceptibility of the metal complexes it is confirmed that Zr(IV) and UO_2(VI) metal complexes are diamagnetic in nature as they do not consist of unpaired electrons. The Mn(III) complex has a magnetic moment 4.77 B.M., indicating the presence of four unpaired electrons. Fe(III) has a magnetic moment 6.25 B.M. indicating the high-spin state of Fe(III). The observed values for VO(IV) and Ti(III) complexes are 1.76 and 1.74 B.M. respectively suggesting the presence of one unpaired electron. The higher values may be due to orbital configuration.

Powder x-ray diffraction

The x-ray diffraction study of metal complexes of Zr(IV), Mn(III) and Fe(III) has been done. The x-ray diffractogram of metal complexes was scanned in the range 5-100° at wavelength 1.543A°. The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). The diffractogram of Zr(IV) complex had thirteen reflections with maxima at $2\theta=24.716^{\circ}$ corresponding to d value 3.599A°. The diffractogram of Mn(III) complex shows thirteen reflections with maxima at $2\theta=36.046^{\circ}$ corresponding to d value 2.4896A°. The diffractogram of Fe(III) complex had fourteen reflections with maxima at $2\theta=24.048^{\circ}$ corresponding to d value 3.6975A°. The x-ray diffraction pattern of these complexes with respect to major peaks having relative intensity grater than 10% have been indexed by using computer programme[28]. The above indexing method also yields miller indices (hkl), unit cell parameters and unit cell volume The Zr(IV) metal complex shows lattice parameter values, a=14.6834A°, b=5.1812A°, c=13.1227A°, $\alpha=\gamma=90^{\circ}$, $\beta=99.82^{\circ}$ and volume V=352.19A$^{\circ 3}$. The observed density is 2.2083gcm^{-3} and calculated density is 2.6601gcm^{-3}. The porosity percentage calculated from the observed and calculated densities is about 0.102. The standard deviation is about 0.018%. The crystal having 8 molecules per unit cell with probable space group $P2_1/C$. In concurrence with these cell parameters, the condition such as $a\neq b\neq c$ and $\alpha=\gamma=90^{\circ}\neq\beta$ required for sample to be monoclinic were tested and found to be satisfactory. This condition was also satisfied for Fe(III) and Mn(III) complexes. The Fe(III) metal complex shows 2 molecules per unit cell having space group C2/c. The lattice parameter values are, a=8.2938A°, b=4.1525A°, c=6.5908A° and $\alpha=\gamma=90^{\circ,}$ $\beta=101.60^{\circ}$ and volume V=222.35A$^{\circ 3}$. The observed standard deviation is 0.031% which is within the permissible limit. The observed and calculated densities from Z values are 1.1266gcm^{-3} and 1.0658gcm^{-3}. The porosity percentage is 0.0569. The lattice parameters for Mn(III) metal complex are a=18.6757A°, b=3.3330A°, c=8.1586Å and $\alpha=\gamma=90^{\circ}$, $\beta=111.06^{\circ}$ and volume V=473.912A$^{\circ 3}$, which supports monoclinic crystal system with 8 molecules per unit cell having probable space group $P2_1/C$. The observed and calculated densities for Mn(III) complexes are 1.3840 gcm^{-3} and 1.6672gcm^{-3}. The porosity percentage is 0.1026. The standard deviation is found to be 0.011%. From the comparison of experimental and theoretical density values, this shows good agreement within the limits of experimental error[29].

Anti-bacterial activity

The antibacterial activity was estimated on the basis of the size of the inhibition zone around the discs. All the obtained results are given in TABLE 4. The results reveal that the activity of the ligand was appreciably enhanced on complexation with the metal. The results were interpreted according to the Cappuceino and Sherman method[30]. This may be explained by the chelation theory[31,32]. According to which, chelation reduces the polarity of the central metal atom because groups and possible π-electron delocalization within the whole chelating ring. This chelation increases the lipophilic nature of the central atom, which favors the penetration of the complexes through the lipid layer of the cell membrane[32,33] and blocking of metal binding sites on the enzymes of the micro-organism.

It is observed from antimicrobial *screening* studies

TABLE 4 : Anti- bacterial activities of β-diketone and its metal complexes

Compound 1mg/0.02 ml	Zone of Inhibition (in mm)				
	B.subtilis	*S.aureus*	*E.coli*	*P.aeruginosa*	*S.typhi*
Streptomycin (Control)*	-----	-----	-----	------	-----
HL	12	R	R	R	R
$Fe[(LH)_2(H_2O)(Cl)]$	15	12	R	23	10
$Mn[(LH)_2(H_2O)(OAc)]$	12	R	R	15	R
$Ti[(LH)_2 (H_2O)(Cl)]$	R	R	R	R	R
$VO[(LH)_2]$	14	R	R	15	R
$UO_2[(LH)_2]$	R	R	R	13	R
$Zr[(LH)_2(H_2O)_2]$	R	12	R	R	R

***No effect upto 24 h, R-Resistant.**

TABLE 5 : Anti- fungal activities of β-diketone and its metal complexes (in mg)

Compound/complex	*A. flavus*		*A. niger*		*A. ustus*		*A. fumigatus*		*A. glaucus*	
	125ppm	250ppm	125ppm	250ppm	125ppm	250ppm	125ppm	250ppm	125ppm	250ppm
DMF (Control)*	32	32	32	32	32	32	32	32	32	32
HL	24	23	26	26	25	23	22	23	22	22
Fe[$(LH)_2(H_2O)(Cl)$]	13	12	14	15	13	12	11	12	08	09
Mn[$(LH)_2(H_2O)(OAc)$]	11	09	12	13	12	13	10	08	10	11
Ti[$(LH)_2$ $(H_2O)(Cl)$]	13	14	12	13	13	13	12	13	10	11
VO[$(LH)_2$]	10	11	11	12	12	13	10	09	08	09
$UO_2[(LH)_2]$	12	14	14	13	12	12	14	13	15	16
Zr[$(LH)_2(H_2O)_2$]	14	13	15	14	13	12	12	11	13	14

that the metal chelates have higher activity than the corresponding free ligand and control against the same microorganisms under identical experimental conditions, which is consistent with earlier reports[34].

As a result, metal complexes of Fe(III), Mn(III) and VO(IV) shows good antibacterial activity whereas Zr(IV) and UO_2(VI) complexes shows comparatively less activity.

Anti-fungal activity

Fungicidal activity of the ligand and it's corresponding metal complexes, their effect on the growth of fungi were studied for the fungi belonging to family, *Aspergillus* and their five different species *i.e. A. flavus, A. niger, A. ustus, A. fumigatus* and *A. glaucus* and given in TABLE 5. The ligand exhibited 30-40% inhibition. Due to synergistic combination of the coordinated metal ions with the ligands, the inhibition by metal complexes has been increased to 40-80% and 60-99% for 125 and 250ppm concentration, respectively.

The antifungal data reveals that the metal complexes show enhanced activity as compared to free ligand and the inhibition increased as the concentration increased. It is found that these complexes show strong antifungal activity at lower concentration as similar to earlier reported literature[34].

From the experiment it is found that VO(VI) and Mn(III) are more inhibitory for growth of fungus. A metal complex of Mn(III) shows more inhibition for *A. flavous* and *A. glaucus* and *A. ustus*.

CONCLUSION

The O-O type β-diketone ligand is synthesized from 2-hydroxy acetophenone and 3,4-Dimethoxy benzoic acid. It acts as a bidentate ligand and forms stable complexes with transition metal ions such as UO_2(VI), Mn(III), Ti(III), Fe(III), VO(IV) and Zr(IV) complexes. The ligand and its complexes are characterized using spectral and analytical data. From the spectral and stoichiometric analyses, a square-pyramidal geometry is assigned for VO(IV) and Mn(III) metal complexes while octahedral geometry is suggested for remaining others. From the XRD study, it is confirmed that Zr(IV), Mn(III) and Fe(III) shows monoclinic systems. The proposed structures for all the metal complexes are given in Figure 1. The complexes are biologically active and exhibit enhanced anti-

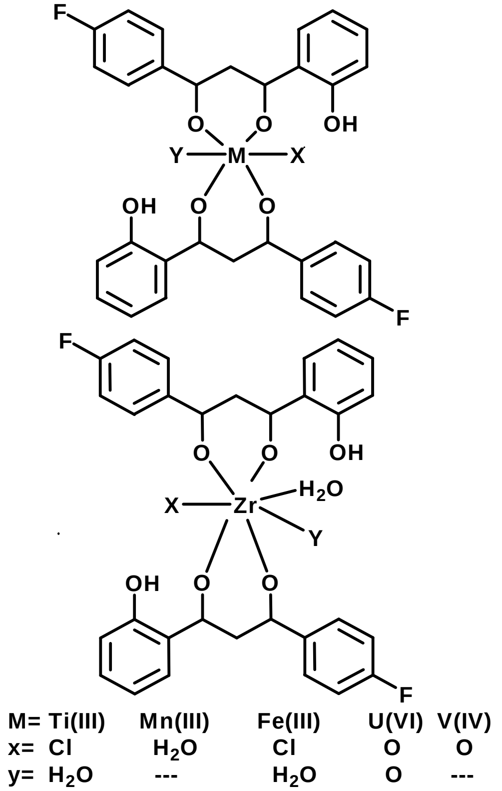


Figure 1 : Proposed structures for the metal complexes

microbial activities as compared to their parent ligand.

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