

SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES DERIVED FROM SOME BIOLOGICALLY ACTIVE FUROIC ACID HYDRAZONES

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ABSTRACT. Two new physiologically active ligands, *N'*-2-(*E*)-1-hydroxy-4-methyl-2-oxo-2H-8-chromenyl ethylidene)-2-furan carbohydrazide (HMCFCFCH) and *N'*-2-[(*Z*)-1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-2-yl) ethylidene]-furan carbohydrazide (HMPFCFCH) and their VO(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes have been prepared. The ligands and the metal complexes have been characterized by elemental analyses, electrical conductance, magnetic susceptibility measurements, UV-Vis, IR, and ESR spectroscopic data. Basing on the above data, Fe(II) and Co(II) complexes of HMCFCFCH and HMPFCFCH have been assigned a dimeric octahedral geometry. VO(II) complexes of HMCFCFCH and HMPFCFCH have been assigned sulfate bridged dimeric square pyramidal geometry. Mn(II) complex of HMCFCFCH has been assigned a dimeric octahedral geometry, where as Mn(II) complex of HMPFCFCH has been ascribed to monomeric octahedral geometry. Cu(II) and Ni(II) complexes of HMCFCFCH have been ascribed to a polymeric structure. Ni(II) complex of HMPFCFCH has been assigned a dimeric square planar geometry. Cu(II) complex of HMPFCFCH has been proposed an octahedral geometry. The ligands and their metal chelates were screened against *S. aureus* and *P. aeruginosa*. The ligands and the metal complexes have been found to be active against these microorganisms. The ligands show more activity than the metal complexes.

KEY WORDS: *N'*-2-(*E*)-1-hydroxy-4-methyl-2-oxo-2H-8-chromenyl ethylidene)-2-furan carbohydrazide (HMCFCFCH), *N'*-2-[(*Z*)-1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-2-yl) ethylidene]-furan carbohydrazide (HMPFCFCH), 3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione, 8-Acetyl-4-methyl-Umbelliferone, Furoic acid hydrazide, Anti microbial activity

INTRODUCTION

Furoic acid hydrazones and their metal complexes are of recent interest [1-6]. Hydrazones and their metal complexes show varied applications in the fields such as anti fungal, anti bacterial, anti oxidative and cytotoxic studies [7-10]. They have been found to be potential chemo therapeutic agents [11, 12]. 3-Acetyl-6-methyl-2H-pyran-2, 4(3H)-dione and 8-acetyl-4-methyl-umbelliferone and furoic acid hydrazide together form Schiff bases which are potential chelating agents and exhibit good physiological and biological activities [13, 14]. In Continuation to our recent studies [15], it has been proposed to synthesize and characterize the transition metal complexes derived from some hydrazones.

EXPERIMENTAL

3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione and furoic acid hydrazide are Fluka reagents. They were used as such. 8-Acetyl-4-methyl umbelliferone was synthesized as reported earlier [16, 17]. Metal salts and other reagents used in the investigation were of AnalaR grade. The solvents used were purified before use. Melting points or decomposition temperatures were determined with Bock-Monoscop-Werck-NR instrument. UV-Vis spectra were recorded on a UV-Vis-Near IR Varian Cary 5E instrument. IR spectra (KBr discs) were recorded on Bruker IFS-66V FT-IR spectrophotometer. ¹H NMR spectra were recorded on NMR Jeol-GSX-400 MHz spectrometer. Electrical conductivities of the metal complexes were studied at room temperature with freshly

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prepared 1 mM solutions in DMSO using Systronics model No: 304 conductivity meter. ESR spectra were recorded as powder on a Varian EPR-E-112 spectrometer. TG and DT analyses were recorded on NETZSCH TGA-DTA/DSC instrument. Metal estimations were carried out using a Varian Spectra AA-20 plus atomic absorption spectrometer. The magnetic susceptibility measurements were carried out by Guoy method at room temperature using $[\text{Hg}(\text{Co}(\text{SCN})_4)]$ as a calibrant. Carbon, hydrogen and nitrogen were determined by microanalyses at CDRI, Lucknow, India.

Preparation of the ligand HMCFCFCH. The ligand HMCFCFCH was prepared by mixing 4-methyl-8-acetyl umbelliferone (0.218 g, 1 mmole) in 20 mL methanol with furoic acid hydrazide (0.126 g, 1 mmole) in 20 mL methanol in a 1:1 proportion. The two solutions were heated under reflux for 4 h. After cooling over night, a yellowish crystalline compound separated out. It was recrystallized from methanol. Yield (49.6 %), m.p. 250 °C.

Preparation of the ligand HMPFCH. The ligand HMPFCH was prepared by mixing 3-acetyl-6-methyl-2H-pyran-2,4(3H) dione (0.168 g, 1 mmole) in 20 mL methanol with furoic acid hydrazide (0.126 g, 1 mmole) in 20 mL methanol in a 1:1 proportion and the two solutions were heated under reflux for 4 h. After cooling overnight, a yellowish crystalline compound separated out. It was recrystallized from methanol. Yield (48.5 %), m.p. 217 °C.

Preparation of the complexes of HMCFCFCH. In the preparation of Mn(II), Co(II), Ni(II) and Cu(II) complexes, the respective metal chlorides (1 mmole) in 10 mL of methanol were heated under reflux with 2 mmoles of HMCFCFCH (0.652 g) in 15 mL of methanol. The mixture was heated under reflux for 4 h. The pH of the reaction was adjusted to 8 using aqueous ammonia solution and the solution was further heated under reflux for two more hours. The metal chelates were separated out upon cooling over night. In the preparation of Fe(II) and VO(II) complexes, ferrous ammonium sulfate and vanadyl sulfate were used. The metal salts were dissolved in aqueous methanol medium. The ligand and the metal salts were taken in the ratio of 2:1 and they were heated under reflux for 4 h. Upon over night cooling the solutions, the metal chelates separated out. The metal complexes separated out were filtered through the sintered glass crucible and were successively washed with water, methanol and pet ether (60-80 °C) and they were dried in vacuum.

Preparation of the complexes of HMPFCH. In the preparation of Mn(II), Co(II), Ni(II) and Cu(II) complexes the respective metal chlorides (1 mmole) in 10 mL of methanol were heated under reflux with 2 mmoles of (0.552 g) HMPFCH in 15 mL of methanol for around 4 h. The pH of the reaction solution was adjusted to 8 using aqueous ammonia solution and the solution was further heated under reflux for two more hours. The metal complexes were separated out upon cooling. In the synthesis of Fe(II) and VO(II) complexes ferrous ammonium sulfate and vanadyl sulfate were used, respectively and the metal salts were dissolved in aqueous methanol medium. The ligands and metal salts were taken in 2:1 ratio and they were heated under reflux for 4 h. Upon cooling the solutions overnight, the metal chelates were separated out. The metal chelates thus isolated were filtered through the sintered glass crucible. They were successively washed with aqueous methanol and pet-ether (60-80 °C) and dried in vacuum.

RESULTS AND DISCUSSION

The analytical data of the ligands and their metal complexes are given in Table 1 and it is in good agreement with the proposed structures and geometries of the ligands and complexes,

respectively. All the metal complexes (Table 2) are colored, stable to air at room temperature and are non-hygroscopic. They decompose without melting above 300 °C. The complexes are insoluble in water, methanol, and acetone and are fairly soluble in dimethyl formamide and dimethyl sulfoxide. All the metal chelates show residual conductance values (10-29 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in $1 \times 10^{-3} \text{ M}$ DMF solution, indicating that they are non-electrolytes (Table 2).

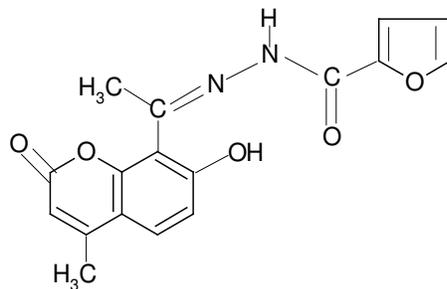
Table 1. Analytical data of the complexes and ligands.

Ligand/complex	Found (calcd) %				
	Metal	Carbon	Hydrogen	Nitrogen	Sulfur
HMCFCH ($\text{C}_{17}\text{H}_{14}\text{O}_5\text{N}_2$)	-	62.57 (61.66)	4.29 (4.59)	8.58 (9.04)	-
[VOHMCFCH] $_2$ SO $_4$	11.74 (11.61)	46.52 (46.48)	2.78 (2.73)	6.42 (6.38)	3.71 (3.65)
[MnHMCFCH.2H $_2$ O] $_2$	13.32 (13.24)	49.24 (49.16)	3.89 (3.86)	6.81 (6.75)	-
[FeHMCFCH.2H $_2$ O] $_2$	13.52 (13.43)	49.12 (49.06)	3.92 (3.85)	6.79 (6.73)	-
[CoHMCFCH.2H $_2$ O] $_2$	14.16 (14.07)	48.83 (48.70)	3.87 (3.82)	6.71 (6.68)	-
[NiHMCFCH] $_n$	15.40 (15.34)	53.42 (53.31)	3.21 (3.14)	7.43 (7.32)	-
[CuHMCFCH.H $_2$ O.Cl]	14.43 (14.41)	46.31 (46.26)	3.22 (3.17)	6.37 (6.35)	-
HMPFCH ($\text{C}_{13}\text{H}_{12}\text{O}_5\text{N}_2$)	-	56.52 (56.21)	4.34 (4.12)	10.14 (10.71)	-
[VOHMPFCH] $_2$ SO $_4$	12.57 (12.49)	38.31 (38.24)	3.24 (3.19)	6.95 (6.88)	3.98 (3.92)
[MnHMPFCH] $_2$	9.16 (9.08)	51.67 (51.58)	3.71 (3.64)	9.38 (9.26)	-
[FeHMPFCH.2H $_2$ O] $_2$	15.29 (15.22)	42.64 (42.53)	4.17 (4.09)	7.71 (7.63)	-
[CoHMPFCH.2H $_2$ O] $_2$	15.56 (15.47)	42.47 (42.40)	4.17 (4.08)	7.69 (7.61)	-
[NiHMPFCH] $_2$	17.69 (17.64)	46.98 (46.89)	3.13 (3.01)	8.54 (8.42)	-
[CuHMPFCH] $_2$	10.39 (10.35)	50.96 (50.85)	3.66 (3.59)	9.24 (9.13)	-

Table 2. Physical characteristics and conductivity data of metal complexes and ligands.

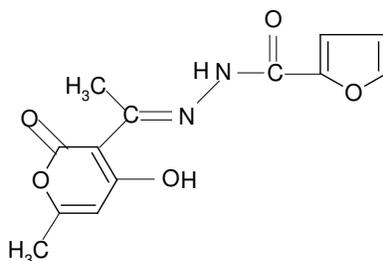
Ligand/complex	Color	Melting/decomposition temperature, °C	Yield (%)	$\Lambda_m (\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
HMCFCH	Light yellow	250	49.6	-
[VOHMCFCH] $_2$ SO $_4$	Light green	>350	51.5	21.4
[MnHMCFCH.2H $_2$ O] $_2$	Light brown	>360	52.0	20.8
[FeHMCFCH.2H $_2$ O] $_2$	Red	>350	51.5	22.3
[CoHMCFCH.2H $_2$ O] $_2$	Red	>360	48.0	27.3
[NiHMCFCH] $_n$	Pinkish red	>350	52.0	28.3
[CuHMCFCH.H $_2$ O.Cl]	Yellowish green	>350	59.0	16.7
HMPFCH	Light yellow	>217	48.5	-
[VOHMPFCH] $_2$ SO $_4$	Yellow brown	>340	61.0	15.3
[MnHMPFCH] $_2$	Light brown	>350	52.5	14.8
[FeHMPFCH.2H $_2$ O] $_2$	Red	>360	56.0	14.2
[CoHMPFCH.2H $_2$ O] $_2$	Red	>360	45.0	13.7
[NiHMPFCH] $_2$	Pinkish red	>360	46.0	10.8
[CuHMPFCH] $_2$	Yellowish green	>360	58.0	15.1

The IR spectra of HMCFCH and HMPFCH exhibit characteristic bands at 3500-3400, 1720-1700, 1670-1660, 1640-1620 and 1470-1310 cm^{-1} which are ascribed to νOH (hydrogen bonded), $\nu\text{C}=\text{O}$ (azide), $\nu\text{C}=\text{N}$ (azomethine) and $\nu\text{C}=\text{O}$ (phenolic), respectively. The infrared frequency at 1080 cm^{-1} in both the ligands is due to $\nu\text{C}-\text{O}-\text{C}$ of the furan ring [18].



HMCFCH

The ^1H NMR spectrum of HMPFCH exhibits the following signals in CDCl_3 : δ 2.18 (s, 3H, $\text{C}_6\text{-CH}_3$), 2.6 (s, 3H, $\text{CH}_3\text{-C=N}$), 5.78 (s, 1H, $\text{C}_5\text{-H}$), 8.2 (s, 1H, CONH), 6.6 (m, 1H, H-2 furoyl), 7.3 (m, 1H, H-3 furoyl), 7.7 (m, 1H, H-4 furoyl) and 11.57 (b, 1H, OH).

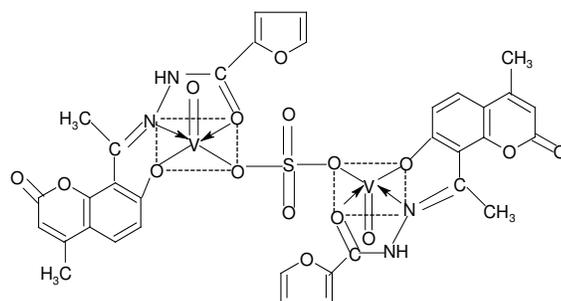


HMPFCH

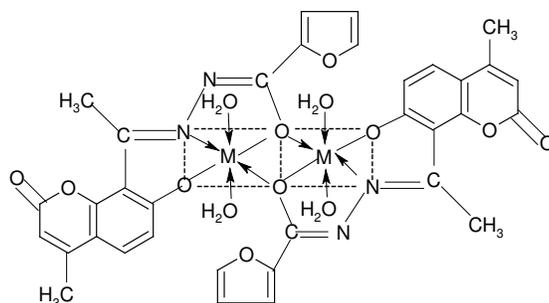
The ^1H NMR spectrum of HMCFCH exhibits the following signals in CDCl_3 : δ 2.2 (s, 3H, $\text{C}_4\text{-CH}_3$), 2.6 (s, 3H, $\text{CH}_3\text{-C=N}$), 6.22 (s, 1H, $\text{C}_3\text{-H}$), 7.58 (s, 1H, $\text{C}_5\text{-H}$), 7.74 (s, 1H, $\text{C}_6\text{-H}$), 8.66 (s, 1H, CONH), 6.95 (m, 1H, H-2 furoyl), 6.27 (m, 1H, H-3 furoyl), 7.33 (m, 1H, H-4 furoyl), 12.13 (b, 1H, OH).

The IR spectra of Mn(II), Fe(II), Co(II) and Ni(II) complexes of HMCFCH do not show the $\nu\text{C=O}$ (azide) IR frequency of the free ligand at $1670\text{-}1660\text{ cm}^{-1}$. It is also supported by the absence of νNH frequency around $3200\text{-}3300\text{ cm}^{-1}$ in metal complexes which supports its enolisation. This is further substantiated by the presence of new non ligand band in the spectra of the complexes around $1270\text{-}1240\text{ cm}^{-1}$, which is due to the enolisation of $\nu\text{C=O}$ (azide) and subsequent deprotonation of enolic OH and the participation of $\nu\text{C-O}$ enolic in complexation [19, 20]. The IR data and the magnetic data of these complexes support the proposed enolic oxygen bridged dimeric structure. The $\nu\text{C=N}$ (azomethine) frequency of the free ligand undergoes a downward shift of $10\text{-}20\text{ cm}^{-1}$ in the spectra of the complexes, indicating the participation of $\nu\text{C=N}$ azomethine nitrogen in coordination [21]. The upward shift of $\nu\text{C-O}$ (phenolic) frequency in the spectra of complexes by $10\text{-}30\text{ cm}^{-1}$ indicates the participation of oxygen of phenolic group in complexation after deprotonation [22]. Mn(II), Fe(II) and Co(II) complexes of HMCFCH show an enolic oxygen bridged dimeric structure. This is further evidenced by the presence of new non ligand peaks at 1150 and 780 cm^{-1} . The coordination of water molecules in the axial positions is supported by the presence of new medium intensity bands at $850\text{-}830\text{ cm}^{-1}$. In the spectrum of Ni(II) complex of HMCFCH a downward shift in

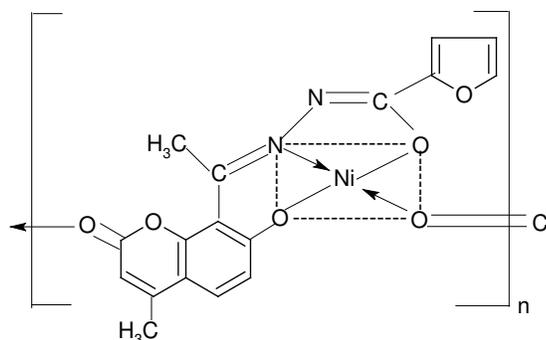
$\nu\text{C}=\text{O}$ (lactone) to the extent of 25 cm^{-1} is observed. This supports the participation of lactone carbonyl in complexation. It leads to the proposal of a polymeric structure to the Ni(II) complex of HMCFCH. In the spectra of VO(II) and Cu(II) complexes of HMCFCH, the $\nu\text{C}=\text{O}$ (azide) around $1670\text{--}1660\text{ cm}^{-1}$ is intact and goes down by $10\text{--}15\text{ cm}^{-1}$ indicating its participation in complexation [23]. In the spectrum of VO(II) complex of HMCFCH the presence of non ligand bands around 990 , $1160\text{--}1050$ and $650\text{--}590\text{ cm}^{-1}$ are attributed to a sulfate bridged dimeric structure [24]. In the IR spectra of all the complexes $\nu\text{C}=\text{N}$ (azomethine) and $\nu\text{C}-\text{O}$ (phenolic) of free ligand undergo downward shift, proving the participation of nitrogen of $\nu\text{C}=\text{N}$ (azomethine) and oxygen of $\nu\text{C}-\text{O}$ (phenolic) in complexation. The IR spectrum Cu(II) complex of HMCFCH shows an absorption band at 320 cm^{-1} which is due $\nu\text{Cu}-\text{Cl}$ [18]. This shows the participation of Cl in complexation. The downward shift of $\nu\text{C}=\text{O}$ (lactone) supports the participation of oxygen of $\nu\text{C}=\text{O}$ (lactone) in coordination. The Ni(II) complex of HMCFCH exhibits a polymeric square planar geometry and the Cu(II) complex of HMCFCH shows a polymeric octahedral geometry. On the whole the Mn(II), Fe(II), Co(II) and VO(II) complexes of HMCFCH show a dimeric structure whereas the Cu(II) and Ni(II) complexes of the above ligand show a polymeric disposition [25].



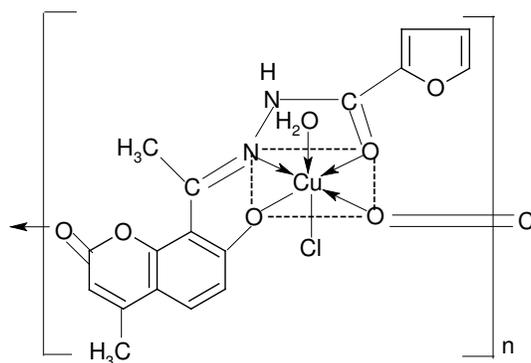
VO(II) complex of HMCFCH



Complexes of HMCFCH, where M = Mn(II), Fe(II) and Co(II)



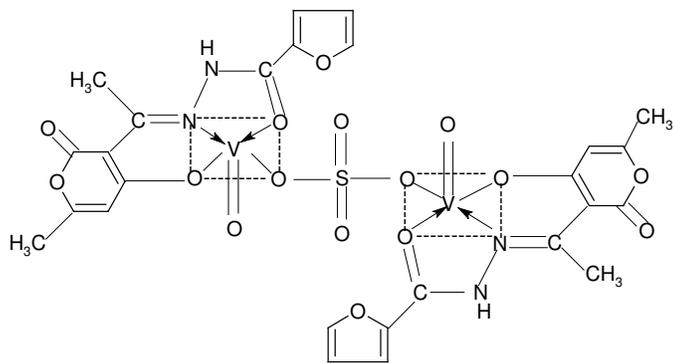
Ni(II) complex of HMCFCH



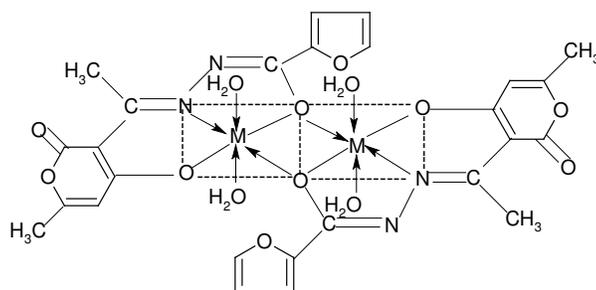
Cu(II) complex OF HMCFCH

The IR spectra of all the complexes of HMPFCH show a downward shift of 20 cm^{-1} in $\nu\text{C}=\text{N}$ (azomethine) indicating the participation of nitrogen of $\nu\text{C}=\text{N}$ (azomethine) in complexation. The upward shift of $\nu\text{C}-\text{O}$ (phenolic) at $1450\text{-}1500\text{ cm}^{-1}$ in the spectra of complexes indicate the participation of phenolic oxygen in coordination [18]. In the spectra of Ni(II), Fe(II) and Co(II) complexes of HMPFCH, the $\nu\text{C}=\text{O}$ (azide) at $1670\text{-}1660\text{ cm}^{-1}$ is absent and the νNH around $3200\text{-}3300\text{ cm}^{-1}$ is also absent, indicating the enolisation of $\nu\text{C}=\text{O}$ (azide) [21]. This is supported by a non ligand band due to $\nu\text{C}-\text{O}$ (enolic) at $1270\text{-}1240\text{ cm}^{-1}$. In view of the above evidences enolic oxygen bridged dimeric square planar geometry is proposed for Ni(II) complex. With two water molecules in the axial position, a dimeric octahedral structure is proposed for Fe(II) and Co(II) complexes of HMPFCH. The presence of water molecules is supported by non-ligand bands at $830\text{-}850\text{ cm}^{-1}$. The IR spectra of VO(II) complex of HMPFCH shows non-ligand bands around $1050\text{-}1160\text{ cm}^{-1}$ and $510\text{-}650\text{ cm}^{-1}$ which are due to sulfate bridged square pyramidal geometry. In the spectra of Cu(II), VO(II), and Mn(II) complexes of HMPFCH the $\nu\text{C}=\text{O}$ (azide) at $1670\text{-}1660\text{ cm}^{-1}$ is intact and goes down by $15\text{-}20\text{ cm}^{-1}$ indicating its participation in complexation [25]. The presence of νNH around $3200\text{-}3300\text{ cm}^{-1}$ in the spectra of these complexes indicates the keto form of the azide moiety. This supports the non-enolisation of $\nu\text{C}=\text{O}$ (azide). The spectra of Cu(II) and Mn(II) complexes of HMPFCH exhibit

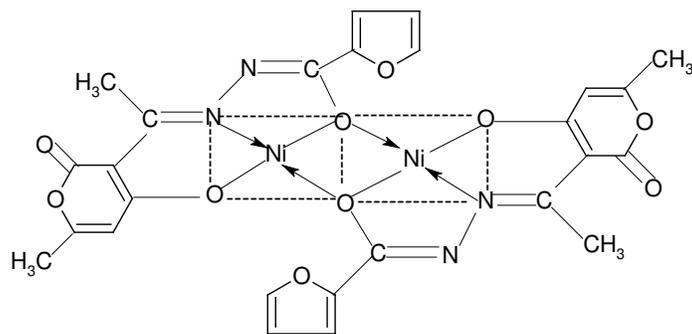
an octahedral geometry with the participation of the nitrogen of azomethine, oxygen of $\nu\text{C}=\text{O}$ (azide) and oxygen of $\nu\text{C}-\text{O}$ (phenolic) in coordination with a 1:2 metal ligand ratio [21]. The spectrum of VO(II) complex suggests a sulfate bridged dimeric square pyramidal geometry.



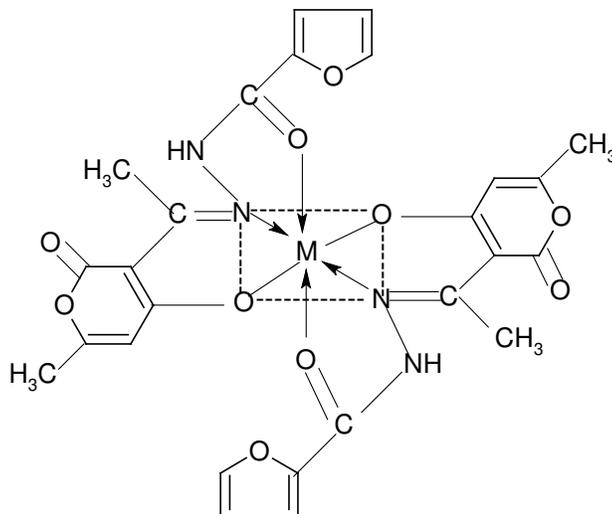
VO(II) complex of HMPFCH



Complexes of HMPFCH, where M = Fe(II) and Co(II)



Ni(II) complex of HMPFCH



Complexes of HMPFCH, where M = Mn(II) and Cu(II)

Thermogravimetric analyses of metal complexes of HMCFCCH ascertain the presence of coordinated water. In case of Mn(II), Co(II) and Fe(II) complexes, the weight loss is found to be two moles of coordinated water per mole of the complex. The weight loss occurs at 140 °C in a single step. In case of Cu(II) complex of HMCFCCH the weight loss has been found to be one mole of coordinated water per mole of the complex. Weight loss occurs at 150 °C [25]. In case of Fe(II) and Co(II) complexes of HMPFCH, the weight loss has been two moles of coordinated water per mole of the complex and it occurs at 140 °C. The magnetic moments of VO(II) complexes of HMPFCH and HMCFCCH are 1.89 and 1.98 B.M., respectively. They are in good agreement with the sulfate bridged square pyramidal geometry. Fe(II) and Co(II) complexes of HMPFCH and HMCFCCH show magnetic moments which are little less than the normally expected value. It indicates their dimeric nature. The magnetic moments are observed at 3.63, 3.72 B.M. for Co(II) complexes and 4.63 and 4.70 B.M. for Fe(II) complexes. Mn(II) complex of HMCFCCH also exhibit subnormal magnetic moment value at 5.5 B.M., which is due to its dimeric octahedral structure. The lower values can be interpreted to the metal-metal bonding. The Mn(II) complex of HMPFCH possess a spin only magnetic moment value of 5.90 B.M. It is in agreement with the octahedral geometry. The Ni(II) complex of HMPFCH and HMCFCCH show diamagnetism, which is due to their square planar disposition. Red color of complexes supports their square planar disposition. The Cu(II) complexes of both HMCFCCH and HMPFCH show a normal magnetic moment value of 2.01 B.M and 1.98 B.M., which are in accordance with their distorted octahedral arrangement [27].

The electronic spectrum of VO(II) complex of HMCFCCH shows three absorption bands at 12000, 19050 and 24300 cm^{-1} , which are assigned to ${}^2B_2 \rightarrow {}^2E$; ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ transitions. These are in accordance with the proposed square pyramidal geometry [30]. The electronic spectrum of VO(II) HMPFCH complex shows absorption bands at 12500, 17700 and 27397 cm^{-1} which are assignable to ${}^2B_2 \rightarrow {}^2E$; ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ transitions, respectively, in a square pyramidal geometry. The Mn(II) complex of HMCFCCH and HMPFCH exhibit three weak transitions each at 9091, 15385, 26316 cm^{-1} and 8300, 16000 and 24500 cm^{-1} . These are assigned to ${}^6A_{1g} \rightarrow {}^4E_g(D)$, ${}^6A_{1g} \rightarrow {}^4T_{1g}(P)$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$, respectively. The

Fe(II) complexes of HMCFCFCH and HMPFCH exhibit absorptions at 10500 and 11300 cm^{-1} , respectively, which are assigned to a ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition and these are in accordance with the octahedral geometry [29]. The other transitions at 24510 and 29412 cm^{-1} are charge transfer transitions. The electronic spectra of Co(II) complexes of HMCFCFCH and HMPFCH, respectively, show absorption bands at 9174, 15723 and 9132, 17600 cm^{-1} . These are interpreted to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions, respectively [30]. These transitions reveal an octahedral geometry around the Co(II) metal ion. The bands at 23000 and 23148 cm^{-1} are due to charge transfer transitions. The electronic spectrum of Ni(II) complexes of HMCFCFCH and HMPFCH shows two absorption bands each at 20000, 23148, and 19608, 24510 cm^{-1} which are interpreted to ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ transitions, respectively [31]. The transitions comply with the proposed square planar stereochemistry. The electronic spectra of Cu(II) complex of HMCFCFCH and HMPFCH shows intense broad bands at 15337 and 16027 cm^{-1} . These are attributed to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition in a distorted octahedral geometry [32]. The other bands at 22727 and 20921 cm^{-1} are assigned for charge transfer transitions.

ESR spectra of Cu(II) HMCFCFCH and Cu(II) HMPFCH were recorded at room temperature as powder. The spectra show g_{av} values 2.09 and 2.092, respectively, which are consistent with their octahedral geometries.

Anti microbial studies

Determination of susceptibility of microorganisms to the ligands and complexes was carried out by paper disc plate method. The procedure is developed by Bayer, Kirby, Sherins and Turk in 1966. In this method the sizes of the zones of inhibition is measured. Filter paper discs, petriplates and all the other apparatus used are sterilized before use. The solvents are dimethyl sulfoxide and methanol. 24 hour old bacterial cultures of *Staphylococcus aureus* (gram +ve), *Pseudomonas aeruginosa* (gram -ve) bacteria, spirit lamp, forceps, incubator and scale were used.

Procedure. 100 mg of test compound is weighed and dissolved in 10 mL of DMSO-methanol medium. From this stock solution 1/10, 1/100, 1/200, 1/300, 1/400 and 1/500 dilutions were prepared in sterile test tubes with DMSO-methanol medium. 40 sterilized Whatman filter paper discs are dipped in each of the above dilute solutions. After soaking for 2 days, the filter paper discs were removed from the solutions and were dried. Nutrient agar plates were prepared. 1 mL of *S. aureus* culture was added in some plates and 1 mL of *P. aeruginosa* culture was added in some other plates. The culture broth is spread in the plates with a sterile spreader. The treated filter paper discs were placed in the inoculated plates using sterile forceps. Different concentrated discs were placed in different plates. They were incubated at 37 $^{\circ}\text{C}$ for 24 h in up right position. The plates were observed after 24 h and the zones of inhibition around the filter paper discs are noted down. The extent of inhibition was measured and the results are given in Table 3 and 4.

The observation of the Tables of biological activity of *S. aureus* and *P. aeruginosa* show that the metalation did not enhance the activity very much except in VO(II) complexes. This may be due to the presence of sulfur in the complex and may be partially due to the square pyramidal geometry. The ligands show more activity than the metal complexes against gram +ve and gram -ve bacteria. No activity has been shown by Mn(II) and Cu(II) complexes of HMPFCH. All the complexes of HMCFCFCH show some activity. The activity in general decreases with the increase in the dilution of the compounds. The activity against *S. aureus* is greater than the activity against *P. aeruginosa*.

Table 3. Anti-microbial studies of the ligands and their metal complexes on *Staphylococcus aureus*.

Compound/concentration	1/10	1/100	1/200	1/300	1/400	1/500
HMCFCH	+++++	+++++	+++	+++	++	+
VO(II)HMCFCH	+++++	+++++	+++	+++	++	+
Mn(II)HMCFCH	+++	+++	+++	++	+	-
Fe(II) HMCFCH	+++	+++	+++	++	+	-
Co(II)HMCFCH	+++	+++	+++	++	+	-
Ni(II)HMCFCH	++++	++++	+++	+++	++	+
Cu(II) HMCFCH	++	++	++	+	-	-
HMPFCH	++++	++++	++++	-	-	-
VO(II)HMPFCH	+++++	+++++	++++	+++	++	+
Mn(II)HMPFCH	+	-	-	-	-	-
Fe(II)HMPFCH	+++	+++	++	++	-	-
Co(II)HMPFCH	+++	+++	++	++	-	-
Ni(II)HMPFCH	+++	++	+	-	-	-
Cu(II)HMPFCH	+	-	-	-	-	-

Table 4. Anti microbial activities of ligands and their metal complexes on *Pseudomonas aeruginosa*.

Compound/concentration	1/10	1/100	1/200	1/300	1/400	1/500
MCFCH	++++	+++	++	++	+	-
VO(II)HMCFCH	++++	+++	+++	+++	+	-
Mn(II)HMCFCH	++	++	++	+	+	-
Fe(II) HMCFCH	++	++	++	+	+	-
Co(II)HMCFCH	++	++	++	+	+	-
Ni(II)HMCFCH	++++	++++	++	+	+	+
Cu(II) HMCFCH	+	+	+	-	-	-
HMPFCH	+++	+++	++	-	-	-
VO(II)HMPFCH	+++	+++	+++	+	-	-
Mn(II)HMPFCH	-	-	-	-	-	-
Fe(II)HMPFCH	++	++	+	+	-	-
Co(II)HMPFCH	++	++	+	+	-	-
Ni(II)HMPFCH	+++	++	+	-	-	-
Cu(II)HMPFCH	-	-	-	-	-	-

+++++ = Highest activity; ++++ = very high activity; +++ = high activity; ++ = moderate activity; + = some activity; - = no activity.

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