

Mn (II) COMPLEX OF N'-(FURAN-2-CARBONYL) HYDRAZINECARBODITHIOIC ACID METHYL ESTER AND Co (II), Cu (II), Zn (II) AND Fe (III) COMPLEXES OF N'-(PYRIDINE- 4-CARBONYL)-HYDRAZINECARBODITHIOIC ACID BENZYL ESTER: SYNTHESIS, SPECTRAL AND X-RAY CHARACTERIZATION

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Abstract:

The ligands N'-(furan-2-carbonyl)-hydrazinecarbodithioic acid methyl ester (H₂fhcm), N'-(pyridine-4-carbonyl)-hydrazine carbodithioic acid benzyl ester hydrochloride (H₂pchbe·HCl) and complexes [Mn(Hfhcm)₂(*o*-phen)] (**1**), [Cu(H₂pchbe)Cl₂] (**2**), [Co(H₂pchbe)Cl₂] (**3**), [Zn(H₂pchbe)Cl₂] (**4**), and [Fe(Hpchbe)₂Cl(H₂O)] (**5**) have been synthesized. They have been characterized with the aid of elemental analyses, IR, NMR, ES Mass, EPR and magnetic susceptibility data. The ligand H₂pchbe·HCl and complex [Mn(Hfhcm)₂(*o*-phen)] (**1**) were also characterized by single crystal X-ray diffraction data. H₂pchbe·HCl and [Mn(Hfhcm)₂(*o*-phen)] (**1**) crystallized in triclinic and monoclinic system with space group P-1 and P-2₁, respectively. The bonding sites of both ligands in the complexes are the carbonyl oxygen and hydrazinic nitrogen. Complexes [Cu(H₂pchbe)Cl₂] (**2**), [Co(H₂pchbe)Cl₂] (**3**) and [Fe(Hpchbe)₂Cl (H₂O)] (**5**) are paramagnetic possessing square planar, tetrahedral and octahedral geometry, respectively. Molecular geometry from X-ray analysis, geometry optimization, frontier molecular orbital (FMO) analysis have been performed using the density functional theory (DFT) with the B3LYP functional. The complex **1** is paramagnetic and octahedral and its crystal structure is stabilized by weak intermolecular C-H···S interaction occurring between thioether sulfur of one molecule and one methyl hydrogen atom of nearby molecule. The structure of the ligand H₂pchbe·HCl is stabilized by weak N-H···Cl, C-H···Cl and $\pi\cdots\pi$ interactions.

Keywords: Ester complexes; Mn(II), Ni(II), Co(II) Cu(II) and Zn(II) complexes; $\pi\cdots\pi$ interactions, intermolecular hydrogen bonding.

Introduction

The coordination chemistry of nitrogen-sulfur donor ligands such as dithiocarbazates, S-aryl/alkyl esters and thiosemicarbazide and their derivatives containing HNCS moiety, is an emerging and rapidly developing area of research [1-4]. The S-alkyl/aryl esters derived from potassium salts of N-arylhiazine carbodithioates have been found to be more stable towards cyclization as compared to the potassium N-arylhiazine carbodithioates and form stable complexes with transition metal ions [5-7]. Some of these compounds have tunable electronic behavior which may result in nonlinear optical (NLO) materials with unique magnetic and

electrochemical properties [8, 9]. Dithiocarbazate derivatives behave as versatile ligands acting either as monodentate neutral S or N (*via* N2) donors or as bidentate anionic (*via* N3-S or S, S) chelating ligands [10-12]. Metal complexes of sulfur-nitrogen chelating ligands derived from S-alkyl esters of dithiocarbazic acid have been studied over the past two decades [13-22] not only because of their intriguing coordination chemistry, but also because of their pronounced biological activities against microbes, viruses and cancer cells [14-16]. Some Schiff bases of S-alkyl esters of dithiocarbazic acid and their complexes were found to display antifungal and antibacterial properties [17-19]. Although several studies on the syntheses and spectral characterization of metal complexes of dithiocarbazates are reported [13-22], there is no report on the dithioester of N-acyl hydrazine, RC(O)NH-NH-C(S)SR which contain similar -NH-C(=S) moiety as the S-alkyl esters of dithiocarbazic acid. The present paper reports the syntheses, spectral and structural characterization of ligands N'-(furan-2-carbonyl)-hydrazinecarbodithioic acid methyl ester (H₂fcm), N'-(pyridine-4-carbonyl)-hydrazine carbodithioic acid benzyl ester hydrochloride (H₂pchbe·HCl) and their complexes [Mn(Hfcm)₂(*o*-phen)] (1), [Cu(H₂pchbe)Cl₂] (2), [Co(H₂pchbe)Cl₂] (3), [Zn(H₂pchbe)Cl₂] (4), and [Fe (Hpchbe)₂Cl(H₂O)] (5).

Figures and Tables

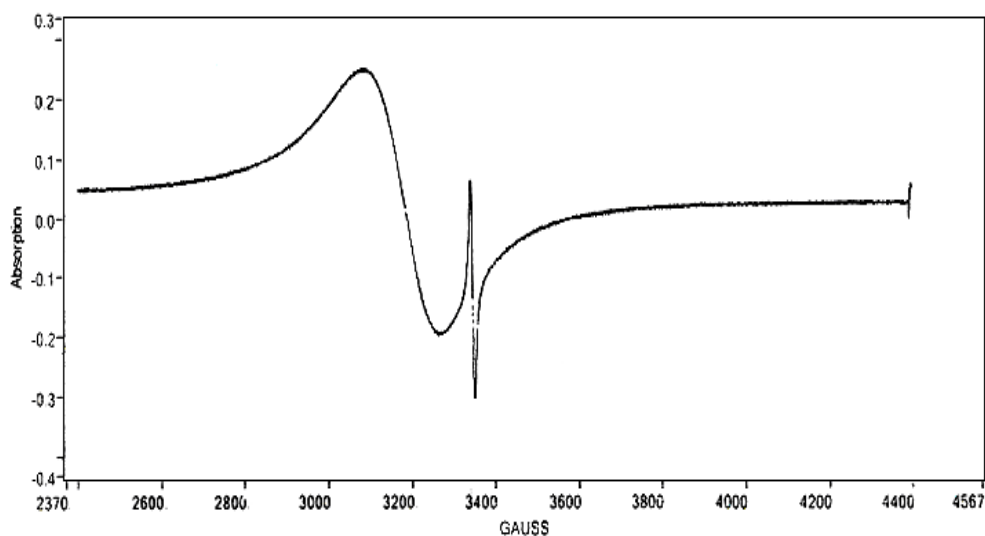


Fig. 1 ESR spectrum of [Cu(H₂pchbe)Cl₂] (2) at room temperature

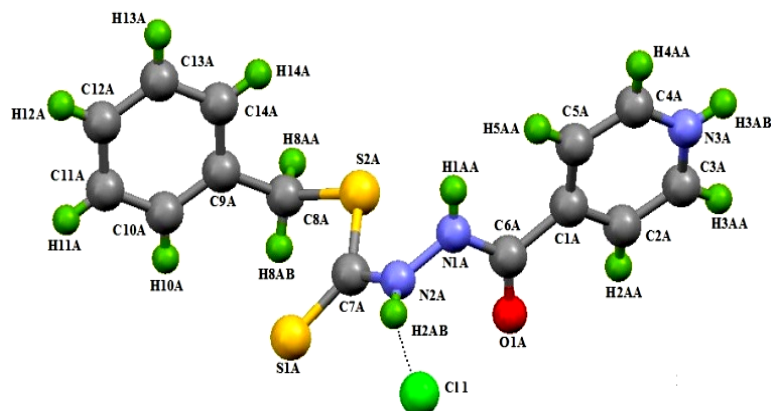


Fig. 2 Molecular structure of H₂pchbe·HCl showing atomic numbering scheme

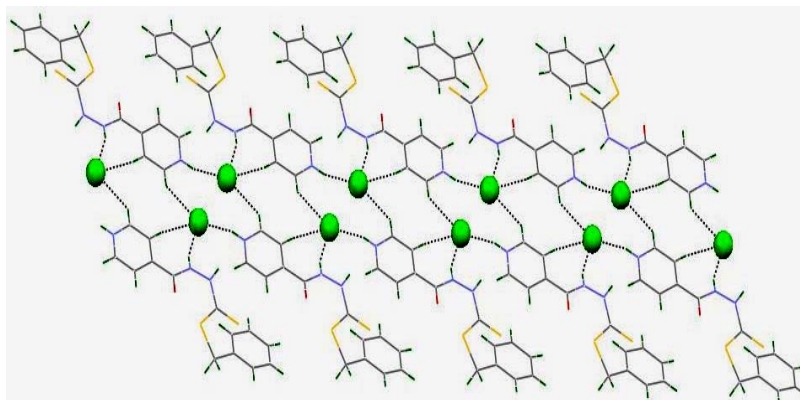


Fig. 3 Close cavities of pyridine rings enclosing a pair of chloride ions in H₂pchbe·HCl

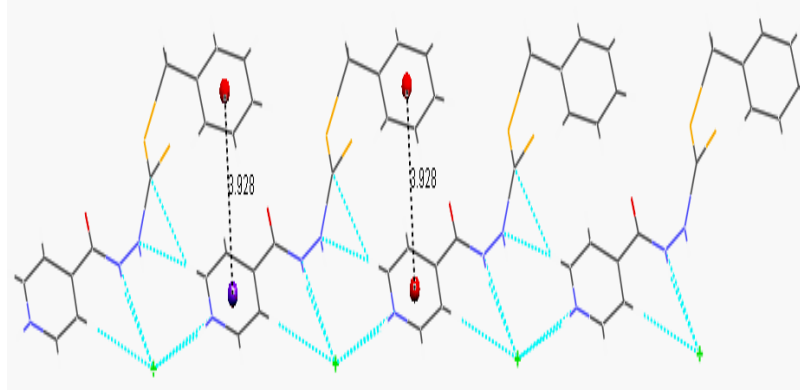


Fig. 4 N-H...Cl hydrogen bonding and π · π interactions between two pyridine ring centroids in H₂pchbe·HCl

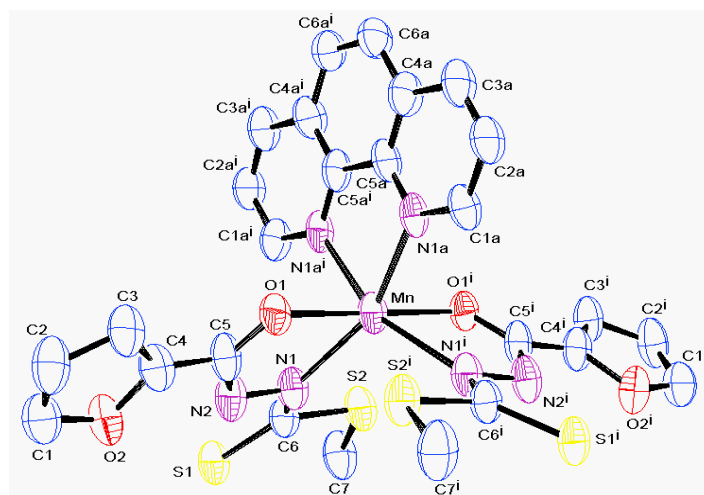


Fig. 5 ORTEP diagram of [Mn(Hfhem)₂(o-phen)] (**1**) showing atomic numbering scheme with ellipsoid of 30 % probability. Hydrogen atoms are omitted for clarity.

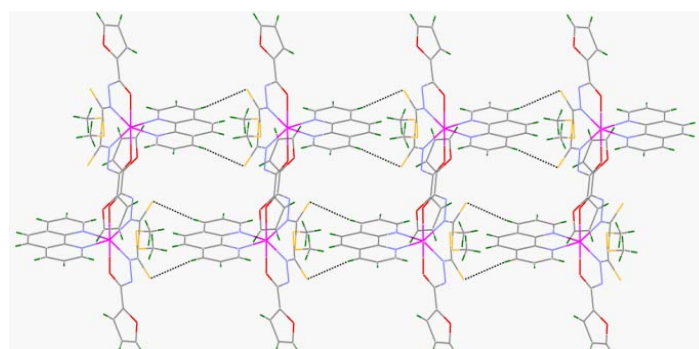


Fig.6 Two dimensional arrangement of the molecules in complex **1** through C-H...S interactions

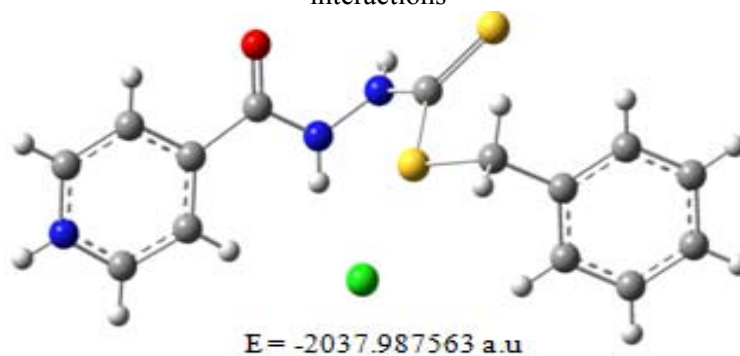


Fig.7. Optimize structure of H₂pchbe·HCl

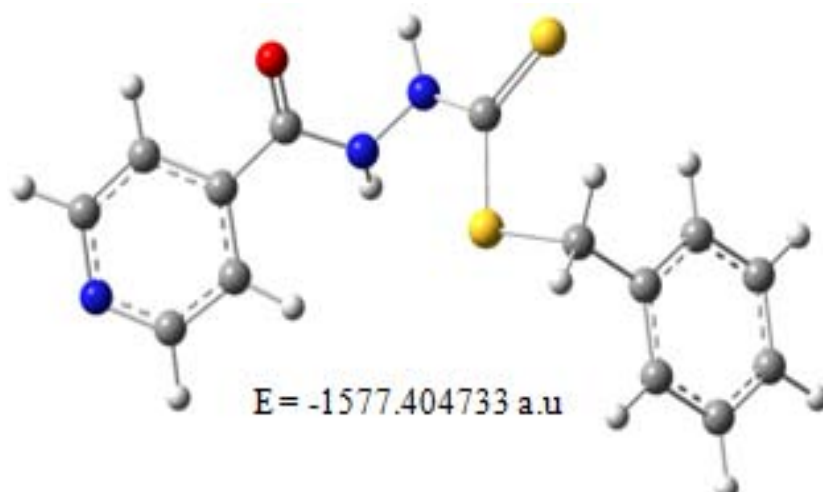


Fig.8. Optimize structure of H₂pchbe

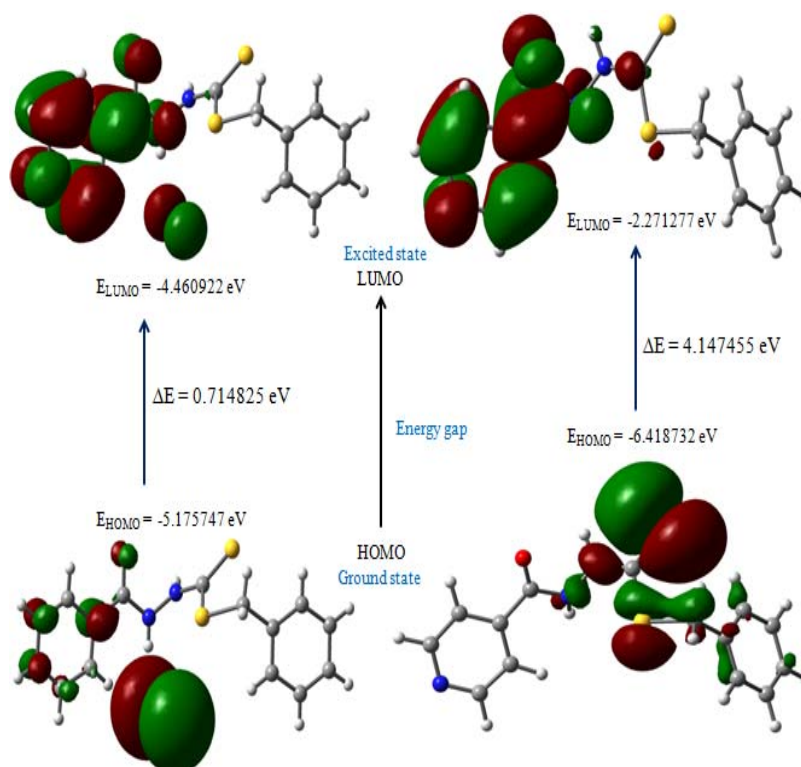


Fig.9 Frontier molecular orbital of H₂pchbe·HCl and H₂pchbe

Table 1 Crystallographic data and structure refinement for H₂pchbe·HCl and complex **1**

Compound	H ₂ pchbe·HCl	Complex 1
Empirical formula	C ₁₄ H ₁₄ ClN ₃ OS ₂	C ₂₆ H ₂₀ MnN ₆ O ₄ S ₄
Formula weight	339.85	663.66
T (K)	200(2)	295(2) K
λ, Mo Kα (Å)	0.71073	1.54178 Å
Crystal system	Triclinic	Monoclinic
Space group	P-1	C 2/c
a (Å)	8.9107(4)	17.001(3)
b (Å)	11.9353(7)	10.4468(12)
c (Å)	15.6285(8)	17.352(2)
α (°)	105.615(5)	90
β (°)	93.996(4)	108.308(15)
γ (°)	90.595(4)	90
V, (Å ³)	1596.15(14)	2925.7(7)
Z	4	4
ρ _{calcd} (g/cm ³)	1.410	1.507
μ (mm ⁻¹)	0.502	6.711
F(000)	700	1356
Crystal size(mm ³)	0.45x0.39x0.32	0.42 x 0.35 x 0.12
θ range for data collections(°)	4.52-34.78	5.04 -76.01
Index ranges	-14 ≤ h ≤ 13 -19 ≤ k ≤ 18 -24 ≤ l ≤ 22	-21 ≤ h ≤ 19 0 ≤ k ≤ 12 0 ≤ l ≤ 21
No. of reflections collected	26640	2890
No. of independent reflections(R _{int})	12786	2890
No. of data /restrains/parameters	12786/0/374	2890 / 0 / 187
Goodness-of-fit on F ²	1.035	2.477
R ₁ ^a , wR ₂ ^b [(I>2σ(I))]	0.0942, 0.2690	0.1367, 0.3893
R ₁ ^a , wR ₂ ^b (all data)	0.1417, 0.2894	0.1892, 0.4698
Largest difference in peak /hole (e.Å ⁻³)	2.478 and -0.473	0.435 and -1.155

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad ^b R_2 = \left[\frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w|F_o|^2} \right]^{1/2}$$

Table 2 Selected bond length (Å) and angle (°) for H₂pchbe·HCl

Bond lengths					
	(Exp.)	(Cal.)		(Exp.)	(Cal.)
S(1A)-C(7A)	1.651(3)	1.630	S(1B)-C(7B)	1.651(3)	1.625
S(2A)-C(7A)	1.756(3)	1.780	S(2B)-C(7B)	1.745(3)	1.739
S(2A)-C(8A)	1.812(4)	1.825	S(2B)-C(8B)	1.810(4)	1.855
O(1A)-C(6A)	1.210 (4)	1.230	O(1B)-C(6B)	1.215(4)	1.230
N(1A)-C(6A)	1.364(4)	1.344	N(1B)-C(6B)	1.359(4)	1.390
N(1A)-N(2A)	1.386(4)	1.355	N(1B)-N(2B)	1.385(4)	1.345
N(2A)-C(7A)	1.349(4)	1.330	N(2B)-C(7B)	1.363(4)	1.326
N(3A)-C(3A)	1.328(6)	1.305	N(3B)-C(3B)	1.335(5)	1.315
N(3A)-C(4A)	1.343(6)	1.360	N(3B)-C(4B)	1.343(5)	1.370
Bond angles					
	(Exp.)	(Cal.)		(Exp.)	(Cal.)
C(7A)-S(2A)-C(8A)	102.1(18)	102.2	C(7B)-S(2B)-C(8B)	102.0(19)	102.6
C(6A)-N(1A)-N(2A)	117.6(3)	116.5	C(6B)-N(1B)-N(2B)	117.4(3)	116.3
C(7A)-N(2A)-N(2A)	122.4(3)	121.4	C(7B)-N(2B)-N(2B)	119.7(3)	120.5
O(1A)-C(6A)-N(1A)	123.4(3)	124.4	O(1B)-C(6B)-N(1B)	122.9(3)	123.4
O(1A)-C(6A)-C(1A)	120.4(3)	121.7	O(1B)-C(6B)-C(1B)	120.7(3)	122.0
N(1A)-C(6A)-C(1A)	116.1(3)	115.3	N(1B)-C(6B)-C(1B)	116.4(3)	115.8
N(2A)-C(7A)-S(1A)	120.8(3)	121.3	N(2B)-C(7B)-S(1B)	120.0(2)	122.5
N(2A)-C(7A)-S(2A)	112.7(2)	110.2	N(2B)-C(7B)-S(2B)	112.9(2)	111.6
S(1A)-C(7A)-S(2A)	126.5(2)	124.4	S(1B)-C(7B)-S(2B)	127.08(19)	126.5
C(9A)-C(8A)-S(2A)	115.4(3)	113.5	C(9B)-C(8B)-S(2B)	115.4(3)	114.4

Table 3 Hydrogen bonds for H₂pchbe·HCl [\AA and $^\circ$]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1A)-H(1AA)...Cl(2)	0.88	2.40	3.229(3)	157.7
N(3A)-H(3AB)...Cl(2)#1	0.88	2.38	3.131(3)	143.6
N(1B)-H(1BA)...Cl(1)	0.88	2.43	3.238(3)	153.6
N(3B)-H(3BB)...Cl(1)#2	0.88	2.31	3.078(3)	146.2
N(2A)-H(2AB)...Cl(1)	0.88	2.45	3.196(3)	142.8
N(2B)-H(2BB)...Cl(2)#3	0.88	2.43	3.189(3)	145.3
C(4B)-H(4BA)...Cl(1)#4	0.95	2.65	3.526(4)	154.4
C(4A)-H(4AA)...Cl(2)#5	0.95	2.66	3.406(4)	136.1
C(5A)-H(5AA)...Cl(2)	0.95	2.76	3.702(4)	171.8

#1 x-1,y,z #2 x+1,y,z #3 x,y+1,z #4 -x+1,-y+1,-z+1 #5 -x,-y,-z+1

Table 4 Selected bond length (\AA) and angle ($^\circ$) for [Mn(HfHCM)₂(*o*-phen)] (1)

Bond lengths		Bond angles	
Mn-O(1)	2.187(9)	O(1)-Mn-O(1)#1	179.5(6)
Mn-N(1A)	2.256(12)	O(1)-Mn-N(1A)	89.3(3)
Mn-N(1)	2.266(11)	O(1)#1-Mn-N(1A)	90.3(4)
O(1)-C(5)	1.234(17)	N(1A)-Mn-N(1A)#1	73.9(5)
O(2)-C(1)	1.355(18)	O(1)-Mn-N(1)#1	105.9(4)
O(2)-C(4)	1.366(18)	N(1A)-Mn-N(1)#1	92.4(4)
N(1)-C(6)	1.301(17)	O(1)-Mn-N(1)	74.4(4)
N(1)-N(2)	1.420(15)	N(1A)-Mn-N(1)	158.8(4)
N(2)-C(5)	1.33(2)	N(1A)#1-Mn-N(1)	92.4(4)
C(6)-S(1)	1.691(12)	N(1)#1-Mn-N(1)	104.8(6)
C(6)-S(2)	1.786(14)	C(5)-O(1)-Mn	114.4(10)
C(7)-S(2)	1.802(17)	N(1)-C(6)-S(1)	126.6(11)

Results and discussion

The ligand N'-(pyridine-4-carbonyl)-hydrazine carbodithioic acid benzyl ester hydrochloride (H₂pchbe·HCl) reacts with metal chlorides to form complexes [M(H₂pchbe)Cl₂] (M = Co, Cu, Zn) and [Fe(Hpchbe)₂Cl(H₂O)] where as the ligand N'-(furan-2-carbonyl)-hydrazine carbodithioic acid methyl ester (H₂fhcm) when treated with manganese(II) acetate and *o*-phen yields [Mn(Hfhcm)₂(*o*-phen)] (**1**). The complexes are stable towards air and moisture. Schemes 1 and 2 depict the formation of the ligands and their complexes. The ligands H₂fhcm and H₂pchbe·HCl are soluble in methanol and ethanol while the complexes **1**, **2**, **3**, **4** and **5** are soluble in DMF and DMSO.

IR spectra

The IR spectrum of N'-(furan-2-carbonyl)-hydrazinecarbodithioic acid methyl ester (H₂fhcm) shows absorptions due to the stretching modes (cm⁻¹) of NH (3200, 3165), C=O (1661), N-N (1080) and C=S (946). The IR spectrum of the complex **1** shows a band at 3149 cm⁻¹ indicating the presence of one NH group upon complexation. The appearance of two new bands for ν(Mn-N) at 441 and 540 cm⁻¹ suggests bonding of Mn(II) with one hydrazinic and *o*-phen nitrogen after loss of a proton. The ν(C=O) and ν(N-N) bands suffer negative and positive shifts of 56 and 24 cm⁻¹, respectively, indicating that H₂fhcm is acting as uninegative bidentate ligand, bonding through carbonyl oxygen and hydrazinic nitrogen in complex **1**. The IR spectrum of N'-(pyridine-4-carbonyl)-hydrazine-carbodithioic acid benzyl ester hydrochloride (H₂pchbe·HCl) shows absorptions (ν cm⁻¹) due to the stretching modes of NH (3,200, 3,101), C=O (1,691), C=S (893) and N-N (1,053) indicating the presence of -C(O)NH-NH-C(S)- group. IR spectra of complexes **2**, **3** and **4** show two bands in the region of 3,160-3,100 and 3,061-3,078 cm⁻¹ showing the presence of both NH groups of the ligand. However, one ν(NH) band at 3,101 cm⁻¹ is found absent in the Fe(III) complex (**5**) indicating loss of one hydrazinic proton. The ν(C=O) and ν(N-N) bands suffer negative and positive shifts of 30-56 and 7-15 cm⁻¹ respectively indicating bonding through carbonyl oxygen and hydrazinic nitrogen in all the complexes. Thus, the ligand acts as a neutral bidentate, bonding through carbonyl oxygen and one hydrazinic nitrogen in the complexes except that of Fe(III) complex, where it acts as an uninegative bidentate bonding through carbonyl oxygen and one hydrazinic nitrogen after loss of a proton. The bonding through hydrazinic nitrogen is supported by the appearance of a new band due to ν(M-N) in the region of 418-422 cm⁻¹ in the above complexes [23].

¹H and ¹³C NMR spectra

The ¹H NMR spectrum of H₂fhcm exhibits a signal at δ 9.68 ppm for the amide and thioamide protons. Methyl protons signal appears at 1.78 ppm. Three protons of the furan ring appear as multiplet between δ 6.50-7.48 ppm. The ¹³C NMR spectrum of H₂fhcm shows seven signals for seven carbon atoms, of which the signals at δ 196.08 and 154.46 ppm are due to the >C=S and >C=O, carbons, respectively. The signal for

$>CH_3$ carbon is observed at δ 16.02 ppm. The furan ring carbons appear at C3:147.28, C4:144.37, C5:134.00 and C6:115.86 ppm. The 1H NMR spectrum of $H_2pchbe \cdot HCl$ in $DMSO-d_6$ shows signals at δ 11.45 and 3.70 ppm for the amide, thioamide and CH_2 protons respectively. One signal observed at 4.20 ppm is due to the hydrogen chloride proton bound to the pyridine nitrogen. Four protons of the pyridine ring appear as multiplet between δ 7.8 - 8.8 ppm and phenyl ring protons appear as multiplet between δ 6.7-7.50 ppm. The ^{13}C NMR spectrum of $H_2pchbe \cdot HCl$ (**1**) shows signals at δ 202.00, 166.05 and 40.33 ppm due to the $>C=S$, $>C=O$ and CH_2 carbons, respectively. The pyridine and phenyl ring carbons appear in the region of δ 151.15-120.33 and 131.75-128.37 ppm, respectively. The 1H NMR spectrum of $[Zn(H_2pchbe)Cl_2]$ in $DMSO-d_6$ shows signals at δ 10.5 (2H) and 3.5 ppm for the amide, thioamide and CH_2 protons. Four protons of the pyridine ring appear as multiplet between δ 7.9-8.8 ppm and benzyl protons appear as multiplet between δ 6.85- 7.45 ppm. The ^{13}C NMR spectrum of $[Zn(H_2pchbe)Cl_2]$ (**4**) shows signals at δ 200.00, 164.41 and 40.05 ppm due to the $>C=S$, $>C=O$ and CH_2 carbons, respectively. The pyridine and phenyl ring carbons appear in the region of δ 150.62-121.13 and 131.45-128.34 ppm, respectively. The signal due to carbonyl carbon appears at 164.41 ppm for the complex **4** which shows an upfield shift of 2 ppm than the ligand, indicating bonding through the carbonyl oxygen.

Electronic spectra and magnetic moments

$Mn(Hfchce)_2(o-phen)$ (**1**) shows a magnetic moment of 5.9 BM which indicates the presence of five unpaired electrons. It shows one low intensity absorption at 15520 cm^{-1} assigned to the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition characteristic of an distorted octahedral $Mn(II)$ complex. The other two bands observed at 28170 and 38160 cm^{-1} may be assigned to the intraligand/charge transfer transitions. A magnetic moment of 1.80 BM for $[Cu(H_2pchbe)Cl_2]$ (**2**) which indicates the presence of one unpaired electron. The appearance of a broad band around 18520 cm^{-1} assigned to the envelope of the ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{2g}$ and 2E_g transitions suggests a square planar geometry for the complex. The magnetic moment of 4.52 BM for $[Co(H_2pchbe)Cl_2]$ (**3**) suggests the presence of $Co(II)$ in a tetrahedral geometry. Its electronic spectrum shows bands at 16340 , 16695 and 18770 cm^{-1} which may be assigned to the split bands due to the ${}^4A_2 \rightarrow {}^4T_1(P)$ transition characteristic of a tetrahedral $Co(II)$ complex. $[Zn(H_2pchbe)Cl_2]$ (**4**) complex is diamagnetic and shows two high intensity absorptions at 29325 and 34970 cm^{-1} assigned to the intraligand/charge transfer transitions. $[Fe(Hpchbe)_2Cl(H_2O)]$ (**5**) shows a magnetic moment of 5.90 BM which indicates the presence of five unpaired electrons. It shows only a high intensity absorption at 26525 cm^{-1} which may be assigned to the intraligand/charge transfer transition [24].

EPR spectra

The ESR spectrum of the copper complex provides information regarding the metal ion environment. The ESR spectrum of the polycrystalline sample of $[Cu(H_2pchbe)Cl_2]$ (Fig.1) at the room temperature shows a strong signal at 3180 G

yielding $\langle g \rangle$ value of 2.1160 which is normal for a Cu(II) complex with one unpaired electron.

ES mass spectra

ES mass spectrometric analysis of $[\text{Fe}(\text{H}_2\text{pchbe})_2\text{Cl}(\text{H}_2\text{O})]$ (**5**) shows the presence of molecular ion peak at $m/z = [713.5]^+$ corresponding to the molecular weight of the complex **5**. The complex **5** gave several important peaks at m/z 678.5 (35 % intensity), 522.2 (34 % intensity) and 504.3 (20 % intensity) which correspond to the fragments formed from $[\text{Fe}(\text{H}_2\text{pchbe})_2\text{Cl}(\text{H}_2\text{O})]$ after release of Cl, $\text{C}_6\text{H}_5\text{CH}_2\text{CSS}$ and H_2O respectively, from the successive fragments.

Crystal structure description of $\text{H}_2\text{pchbe}\cdot\text{HCl}$

The crystallographic data and structural refinement details for $\text{H}_2\text{pchbe}\cdot\text{HCl}$ are given in Table 1 and selected bond distances and bond angles in Table 2. Hydrogen bonding parameters of the ligand are given in Table 3. Fig 2 shows the molecular structure of the ligand $\text{H}_2\text{pchbe}\cdot\text{HCl}$ with the atomic numbering scheme. The asymmetric unit of $\text{H}_2\text{pchbe}\cdot\text{HCl}$ contains two crystallographically independent molecules labelled A and B with similar geometry. The molecules are arranged in layers, orienting the pyridine rings in such a way that four of the pyridine rings form a cavity. This arrangement leaves the carbonyl oxygen of two adjacent molecules oriented opposite to each other. The above mentioned cavity formed by pyridine rings contains a pair of chloride ions held by $\text{N-H}\cdots\text{Cl}$ and $\text{C-H}\cdots\text{Cl}$ hydrogen bonding formed between hydrazinic hydrogen atom and chloride ion as well as CH hydrogen atom of pyridine ring and chloride ion (Fig. 3). The C-S bond distances of 1.748(4) and 1.661(4) Å (Table 2) in $\text{H}_2\text{pchbe}\cdot\text{HCl}$ agrees well with those in related compounds, being intermediate between 1.82 for a C-S single bond and 1.56 Å for a C=S double bond [25]. The crystal structure is further stabilized by weak $\pi\cdots\pi$ interactions between two pyridine rings and the distance between two pyridine ring centroids is found to be 3.928 Å (Fig.4) which is well within the reported value [26].

Crystal structure description of $[\text{Mn}(\text{Hfhem})_2(\text{o-phen})]$ (**1**)

Fig.5 shows an ORTEP diagram of complex **1** with the atomic numbering scheme. The structural refinement data related to complex **1** are listed in Table 1 and the selected bond distances and bond angles are listed in Table 4. The metal center in complex **1** is coordinated in an N_4O_2 core by two uninegative bidentate ligands using hydrazine nitrogen (N1, after loss of proton) and carbonyl oxygen. The distances found within the chelate rings are intermediate between single and double bond lengths. The average bond lengths in the chelate of complex **1** are: $\text{O1-C5} = 1.234(17)$, $\text{N1-C6} = 1.301(17)$, $\text{N1-N2} = 1.420(15)$, $\text{N2-C5} = 1.330(2)$ Å which suggest considerable delocalization of charge [27, 28]. The N, O donor sites of the bidentate ligand chelates the Mn(II) center to form a five-membered CN_2OMn ring. The resulting complex has a distorted octahedral geometry. The Mn-O bond length in complex **1** is 2.187 Å and the Mn-N bond lengths are 2.266 and 2.256 Å for Mn-N (hydrazinic) and Mn-N (*o-phen*),

respectively. The shorter Mn-N (*o*-phen) bond length as compared to Mn-N (hydrazinic) indicates that the *o*-phen nitrogen bonds more strongly than the hydrazinic nitrogen. The bond angles N(1A)-Mn-N(1) 158.8(4)° and N(1A)-Mn-N(1A)# 73.90(5)° indicate distortion from an ideal octahedral geometry [29]. In the complex **1** the C(5)-N(2) and C(6)-N(1) bond distances show partial double bond character due to delocalization of π electrons throughout the whole chelate ring [30]. Both chelate rings around Mn(II) formed by the (Hfhcm)⁻ are almost orthogonal to each other forming a dihedral angle of 81.36°. In complex, the chelate rings and the furan rings lie nearly in the same plane forming a dihedral angle of 6.61°. The complex **1** is quite stable in solid state due to π electron delocalization and weak intermolecular C-H \cdots S interaction between thioether sulfur of one molecule and *o*-phen ring hydrogen atom of a nearby molecule (Fig.6).

Quantum chemical calculations

Optimization of geometry

All calculations and the geometry optimization of ligand H₂pchbe·HCl and H₂pchbe have been performed with Gaussian 03 and Gauss View 4.1 [31] program packages using DFT method with functional B3LYP and basis set DFT/B3LYP/6-311G(d, p) [32, 33]. The input geometries for the DFT calculations were generated from single crystal X-ray data. The optimized geometrical parameters are listed in Table 2. The input geometry of the H₂pchbe·HCl for the DFT calculations was generated from single crystal X-ray data. The optimized energy H₂pchbe·HCl and H₂pchbe were -2037.987563 and -1577.404743 a.u respectively indicating that the H₂pchbe·HCl is more stable than the H₂pchbe (Figs.7 & 8). The slight disagreement in the bond lengths of H₂pchbe·HCl is due to the fact that the DFT calculations are done for an isolated molecule in gaseous phase while the X-ray crystallographic data were obtained from crystal lattice of the molecule. The optimized geometries of H₂pchbe·HCl and H₂pchbe are shown in Figs 7 and 8. There is good agreement between the geometrical parameters obtained by X-ray crystallography to those generated by DFT method as shown in Table 2.

Frontier molecular orbital (FMO) and NLO analysis

The HOMO-LUMO energy and the energy gap (ΔE) for H₂pchbe·HCl and H₂pchbe have been calculated and are shown in Fig. 9 and can be observed that the HOMO orbital of the two molecule has different orientation but no contribution of HNCS moiety and benzyl ring of H₂pchbe·HCl, the only contribution of electronic density from chloride and pyridinium ion whereas on H₂pchbe, the HNCS moiety has contribution of electronic density to HOMO. The benzyl ring does not make any contribution to LUMO, the only contribution from pyridinium-4-carbonyl side. The HOMO energy of H₂pchbe·HCl is moderate and the LUMO energy is lower than that of H₂pchbe which indicates for electron donating tendency is average but the accepting tendency is higher, which results in small energy gap of H₂pchbe·HCl. The value of the energy separation between the HOMO and LUMO is 0.714825 and 4.147455 eV for

H₂pchbe·HCl and H₂pchbe, respectively. The findings for this molecule imply that the minimum gap value occurs at the geometry which corresponds to the relaxed structure. The small HOMO–LUMO Energy gap, about six times lower than that of H₂pchbe, means low excitation energy for H₂pchbe·HCl, a good stability and a low chemical hardness for the compound. DFT calculation also reveals that the chloride ion play an important role in changing the HOMO–LUMO energy gap of the molecule. The electronic transition from the ground state to the excited state is due to a transfer of electrons from the HOMO to LUMO level is mainly $\pi \rightarrow \pi^*$ transition and small HOMO–LUMO gap requires small excitation energy and so the absorption bands are shifted towards the visible region.

The chemical hardness of a molecule defined by the formula [34].

$$\eta = \{-E_{\text{HOMO}} + E_{\text{LUMO}}\}/2$$

Where E_{HOMO} and E_{LUMO} are the energies of the HOMO and LUMO molecular orbital. The value of η of H₂pchbe·HCl and H₂pchbe are 0.357413 and 2.073727 eV, respectively indicates that H₂pchbe·HCl is soft material and H₂pchbe is about six times harder than that of H₂pchbe·HCl. The above result indicates that H₂pchbe·HCl have better chemical activity, low kinetic stability (a characteristic of soft molecule) and may effectively carry out intramolecular charge transfer upon excitation. Due to the presence of various types of hydrogen bonding and CH \cdots π interaction in H₂pchbe·HCl, electron delocalization becomes easier, which decreases the value of the energy gap, which makes it as a soft material, so the absorption bands in the electronic spectrum of H₂pchbe·HCl is shift to the visible region and consequently, increases the nonlinear optical properties as compared to H₂pchbe·HCl. This suggests that the addition of HCl modify the charge distribution of the structure versus that of the free H₂pchbe.

Experimental

Chemical and starting materials

Commercial reagents were used without further purification and all experiments were carried out in open atmosphere. Benzyl chloride, CS₂ (S D Fine Chemicals, India), KOH (Qualigens), isonicotinic acid hydrazide and furoic acid hydrazide (Sigma Aldrich) were used as received. All the solvents were purchased from Merck Chemicals, India, and used after purification.

Physical measurements

Carbon, hydrogen, nitrogen and sulphur contents were estimated on a CHN Model CE-440 Analyzer and on an Elementar Vario EL III Carlo Erbo 1108.. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using Hg[Co(NCS)₄] as the calibrant. Electronic spectra were recorded on a SHIMADZU 1700 UV-Vis spectrophotometer as Nujol mull. IR spectra were recorded in the 4000–400 cm⁻¹ region as KBr pellets on a Varian Excalibur 3100-FT IR spectrophotometer. ¹H and ¹³C NMR spectra were recorded in *d*₆-DMSO on a JEOL

AL 300 FT NMR spectrometer using TMS an internal reference. ES mass spectrum of $[\text{Fe}(\text{Hpchbe})_2\text{Cl}(\text{H}_2\text{O})]$ (**5**) was recorded on MICROMASS QUATTRO II triple quadrupole mass spectrometer. EPR spectrum of $[\text{Cu}(\text{H}_2\text{pchbe})\text{Cl}_2]$ (**2**) was recorded on an X-band spectrometer model Varian E-112 using DPPH as <g> marker.

X-ray crystallography

Data for the structure of the ligand $\text{H}_2\text{pchbe}\cdot\text{HCl}$ and complex $[\text{Mn}(\text{Hfhcm})_2(o\text{-phen})]$ (**1**) were obtained at 200(2) and 295(2) K, respectively, on a Bruker three-circle SMART 6000 CCD diffractometer using a graphite mono-chromated Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation source. The structure was solved by direct methods (SHELXL-08) and refined against all data by full matrix least-square on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the refinement at geometrically ideal position and refined with a riding model [35]. The MERCURY package was used for molecular graphics [36]. Molecular structure diagrams were generated by use of the ORTEP-3 for Windows program [37]. Complex **1** was a twinned dataset and thus the R value is high.

Synthesis

Synthesis of N'-(furan-2-carbonyl)-hydrazinecarbodithioic acid methyl ester (H₂fhcm)

Potassium N'-(furan-2-carbonyl) hydrazine carbodithioate was prepared by adding CS_2 (2.4 ml, 40 mmol) to a solution of furan-2-carboxylic acid hydrazide (2.52 g, 20 mmol) and potassium hydroxide (1.12g, 20 mmol) in methanol (30 ml) and stirring the reaction mixture for 2 h. The solid that separated was filtered off, washed with 10 % (v/v) mixture of EtOH-ether and dried *in vacuo*. The N'-(furan-2-carbonyl)-hydrazinecarbodithioic acid methyl ester (H_2fhcm) was synthesized by the drop wise addition of methyl iodide (1.0 ml, 15 mmol) to a suspension of freshly prepared above potassium N'-(furan-2-carbonyl) hydrazine carbodithioate (2.40 g, 10 mmol) in methanol (15 ml) and the reaction mixture stirred continuously for 1 h at room temperature and filtered to remove the residue. On evaporation of the solvent and acidification of the product with dil CH_3COOH (20 % v/v), yellow precipitate was obtained. This was suction filtered, washed with water and dried *in vacuo*. The yellow solid was crystallized from MeOH. Yield: 70 %. M.p. 148 °C; Anal. Found: C, 38.75; H, 3.85; N, 12.80; S, 29.75 %. Calc. for $\text{C}_7\text{H}_8\text{N}_2\text{O}_2\text{S}_2$ (216.00): C, 38.88; H, 3.70; N, 12.96; S, 29.62 %. IR ($\nu \text{ cm}^{-1}$, KBr): $\nu(\text{NH})$ 3200m, 3165m; $\nu(\text{C}=\text{O})$ 1661s; $\nu(\text{N}-\text{N})$ 1080s; $\nu(\text{C}=\text{S})$ 946m. ^1H NMR ($\text{DMSO}-d_6$; δ ppm): 9.68 (s,2H, -NH), 6.50-7.48 (3H, furan ring), 1.78 (s,3H, - CH_3). ^{13}C NMR ($\text{DMSO}-d_6$; δ ppm): 196.08 (C=S), 158.46 (C=O), 147.28 (C3), 144.37 (C4), 134.00 (C5), 115.86 (C6), 16.02 (C7) (scheme 1).

Synthesis of N'-(pyridine-4-carbonyl)-hydrazine carbodithioic acid benzyl ester hydrochloride (H₂pchbe·HCl)

The N'-(pyridine-4-carbonyl)-hydrazine-carbodithioic acid benzyl ester hydrochloride was synthesized by the drop wise addition of benzyl chloride (1.5 ml, 10

mmol) to a suspension of freshly prepared potassium N'-(pyridine-4-carbonyl) hydrazine carbodithioate [$K^+(H_2L)$] (2.0 g, 8 mmol) [38] in methanol (15 ml) and the reaction mixture stirred continuously for 2 h at room temperature. The product obtained on evaporation of the solvent was filtered off, washed twice with portions of carbon tetrachloride and acidified the residue with dil. HCl (5.0 ml, 20 % v/v). The residue was washed with H₂O and finally dried *in vacuo*. Colorless single crystals of H₂pchbe·HCl suitable for X-ray analyses were obtained by slow evaporation of an ethanol solution over a period of 10 days. Yield: 70 %. M.p. 185 °C. Anal. Found: C, 49.40; H, 3.95; N, 12.45; S, 18.75 %. Calc. for C₁₄H₁₃ClN₃OS₂ (339.85): C, 49.4; H, 3.8; N, 12.5; S, 18.8 %. ¹H NMR (DMSO-d₆; δ ppm): 11.45 (s, 2H, NH), 4.2 (s, 1H) 7.8 and 8.8 (m, 4H, pyridine); 7.50 (m, 5H, phenyl ring); 3.7 (2H, CH₂); ¹³C NMR (DMSO-d₆; δ ppm): 202 (C7a), 166.05 (C6a), 40.33 (C8a), 151.15 (C4a, C3a), 130.53 (C1a) 120.33 (C5a, C2a), 129.37 (C13a, C11a), 131.75 (C9a), 128.37 (C14a, C10a) (Fig.2). IR (KBr, cm⁻¹): ν(NH) 3,200m, 3,101m, ν(C=O) 1,691s; ν(N-N) 1,053s; ν(C=S) 893m (scheme 2).

Preparation of [Mn(Hfchm)₂(o-phen)] (1)

Mn(OAc)₂·4H₂O (0.244 g, 1 mmol) and H₂fchm (0.432 g, 2 mmol) were dissolved separately in 25 ml methanol, mixed together and stirred for 2 h. The yellow precipitate which separated was filtered, washed successively with ethanol-water mixture (50:50) and air dried. A methanol solution of o-phen (0.200 g, 1mmol) was added to the methanol suspension of the above complex and stirred for 3 h. The resulting clear yellow solution was filtered and kept for crystallization. Yellow single crystals of **1** suitable for X-ray analyses were obtained by slow evaporation of the methanol solution over a period of 9 days. Yield: 58 %; M.p. 260 °C, μ_{eff} = 5.9 BM. Anal. Found: C, 47.10; H, 3.05; N, 12.55; S 19.20, 8.35 %. Calc. for C₂₆H₂₀MnN₆O₄S₄ (663.66): C, 47.01; H, 3.01; N, 12.65; S, 19.28, Mn, 8.28 %. IR (cm⁻¹, KBr): ν(NH) 3149m, ν(C=O) 1605s, ν(N-N) 1095, ν(C=S) 922m, ν(M-N) 421 and 540.

Synthesis of [Cu(H₂pchbe)Cl₂] (2)

CuCl₂·2H₂O (0.170 g, 1 mmol) and H₂pchbe·HCl (0.340 g, 1 mmol) were dissolved separately in 15-20 ml methanol, mixed together and stirred for 1 h. The black solid which separated was filtered, washed successively with ethanol-water mixture (50:50) and air dried. Yield: 60 %. Mp. 289 °C. Anal. Found: C, 38.5; H, 2.9; N, 9.7; S, 14.6 Cu, 14.55 %. Calc. for C₁₄H₁₃N₃Cu OS₂Cl₂ (437.89): C, 38.4; H, 3.0; N, 9.6; S, 14.6, Cu, 14.51 %. IR (KBr, cm⁻¹): ν(NH) 3,160m, 3,078m, ν(C=O) 1,635s; ν(N-N) 1,062s; ν(C=S) 844m; ν(M-N) 418w. μ_B = 1.8 BM.

Synthesis of [Zn(H₂pchbe)Cl₂] (3)

A solution of H₂pchbe·HCl (0.340 g, 1 mmol) in MeOH (10 ml) was added to a MeOH solution (10 ml) of ZnCl₂ (0.136 g, 1 mmol). This mixture was magnetically stirred for 1 h at room temperature. The resulting yellow precipitate was filtered off, washed thoroughly with EtOH and air dried. Yield: 58 %. M.p. 285 °C. Anal. Found:

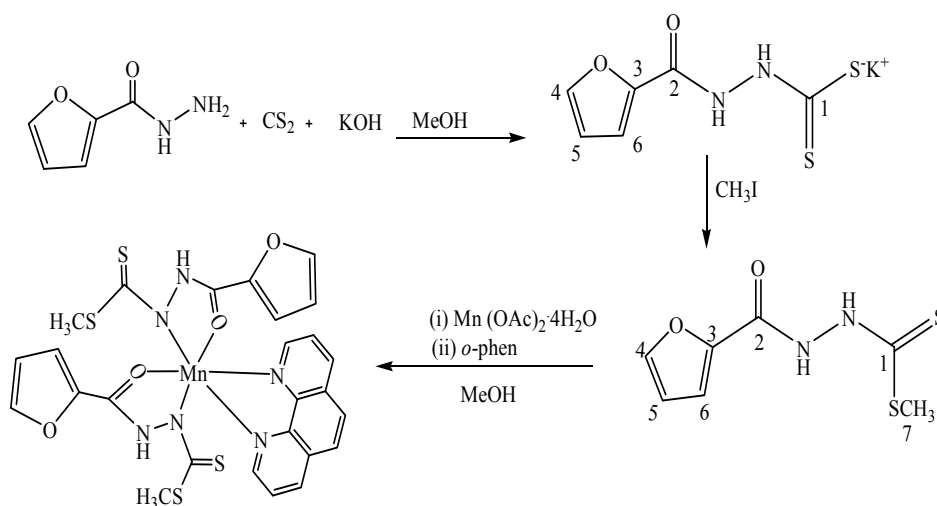
C, 38.3; H, 2.9; N, 9.9; S, 14.5 %. Calc. for $C_{14}H_{13}N_3ZnOS_2Cl_2$ (439.74): C, 38.2; H, 3.0; N, 10.0; S, 14.6 %. 1H NMR (DMSO- d_6 ; δ ppm): 10.5 (s, 1H, NH), 7.9 and 8.8 (m, 4H, pyridine); 7.45 (m, 5H, phenyl); 3.5 (2H, CH_2); ^{13}C NMR (DMSO- d_6 ; δ ppm): 200 (C=S), 164.41 (C=O), 40.05 (CH_2), 150.62 (C4, C3), 130.20 (C1), 121.13 (C5, C2) (pyridine ring), 130.90 (C13, C11), 131.45 (C9), 128.34 (C14, C10) (phenyl ring). IR (KBr, cm^{-1}): $\nu(NH)$ 3,082m, 3,061m, $\nu(C=O)$ 1,655s; $\nu(N-N)$ 1,064s; $\nu(C=S)$ 898m; $\nu(M-N)$ 420w.

Synthesis of $[Co(H_2pchbe)Cl_2]$ (4)

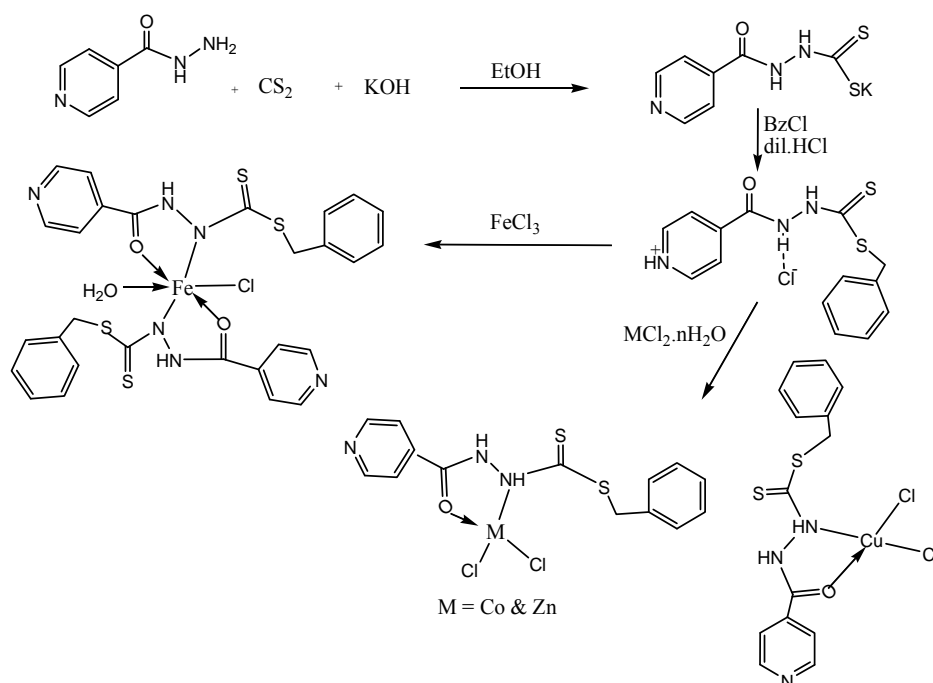
$CoCl_2 \cdot 6H_2O$ (0.237 g, 1 mmol) and $H_2pchbe \cdot HCl$ (0.340 g, 1 mmol) were dissolved separately in 15-20 ml methanol, mixed together and stirred for 1 h. The brown solid which separated was filtered, washed successively with ethanol-water mixture (50:50) and air dried. Yield: 55 %. M.p. 260 °C. Anal. Found: C, 38.7; H, 2.9; N, 9.8; S, 14.7; Co, 13.46 %. Calc. for $C_{14}H_{13}N_3 CoOS_2Cl_2$ (433.28): C, 38.8; H, 3.0; N, 9.7; S, 14.8; Co, 13.54 %. IR (KBr, cm^{-1}): $\nu(NH)$ 3,100m, 3,068m, $\nu(C=O)$ 1,675s; $\nu(N-N)$ 1,065s; $\nu(C=S)$ 885m; $\nu(M-N)$ 422. $\mu_B = 4.5$ BM.

Synthesis of $[Fe(Hpchbe)_2Cl(H_2O)]$ (5)

A solution of $H_2pchbe \cdot HCl$ (0.680 g, 2 mmol) in MeOH (10 ml) was added to a MeOH solution (10 ml) of $FeCl_3$ (0.162 g, 1 mmol). This mixture was stirred for 2 h at room temperature. The resulting black precipitate was filtered off, washed thoroughly with EtOH and air dried. Yield: 58 %. M.p. 220 °C. Anal. Found: C, 47.0; H, 3.5; N, 11.7; S, 17.9 %. Calc. for $C_{28}H_{26}N_6FeO_3S_4Cl$ (714.04): C, 47.1; H, 3.6; N, 11.8; S, 17.9 %. IR (KBr, cm^{-1}): $\nu(OH)$ 3,449; $\nu(NH)$ 3,061; $\nu(C=O)$ 1,674s; $\nu(N-N)$ 1,059s; $\nu(C=S)$ 896m; $\nu(M-N)$ 423w. $\mu_B = 5.9$ BM.



Scheme 1 Preparation of the ligand H_2fcm and its $Mn(II)$ complex



Scheme 2 Preparation of ligand $H_2pchbe \cdot HCl$ and its complexes

Conclusions

This paper reports the syntheses and spectral characterization of the complexes $[Mn(Hfcm)_2(o\text{-phen})]$ (**1**), $[Cu(H_2pchbe)Cl_2]$ (**2**), $[Co(H_2pchbe)Cl_2]$ (**3**), $[Zn(H_2pchbe)Cl_2]$ (**4**), and $[Fe(Hpchbe)_2Cl(H_2O)]$ (**5**) formed by N' -(furan-2-carbonyl)-hydrazinecarbodithioic acid methyl ester (H_2fcm) and N' -(pyridine-4-carbonyl)-hydrazinecarbodithioic acid benzyl ester hydrochloride ($H_2pchbe \cdot HCl$). The ligand $H_2pchbe \cdot HCl$ and complex $[Mn(Hfcm)_2(o\text{-phen})]$ (**1**) have also been characterized by single crystal X-ray analyses. The structure of the ligand $H_2pchbe \cdot HCl$ is stabilized by the $N-H \cdots Cl$ and $C-H \cdots Cl$ hydrogen bonding and $\pi \cdots \pi$ interactions. The bonding sites of the both ligands in the complexes are the carbonyl oxygen and hydrazinic nitrogen. The complexes formed by $Cu(II)$, $Co(II)$ and $Fe(III)$ with H_2pchbe are paramagnetic possessing square planar, tetrahedral and octahedral geometry, respectively. The complex **1** is paramagnetic and octahedral whose crystal structure is stabilized through weak intermolecular $C-H \cdots S$ interaction between thioether sulfur of one molecule and *o*-phen ring hydrogen atom of a nearby molecule. The optimized energy of $H_2pchbe \cdot HCl$ and H_2pchbe were -2037.987563 and -1577.404743 a.u respectively indicating that the $H_2pchbe \cdot HCl$ is more stable than the H_2pchbe . The small HOMO–LUMO energy gap means low excitation energy for the $H_2pchbe \cdot HCl$, a good stability and a low chemical hardness for the compound $H_2pchbe \cdot HCl$ than in

comparison to H₂pchbe. The nonlinear optical property is calculated theoretically and H₂pchbe·HCl may be a potential applicant in the development of NLO materials.

Acknowledgements

One of the authors Dr. M.K. Bharty is thankful to the Science and Engineering Research Board, India for the award of a Project (No. YSS/2015/001201). This paper is dedicated to Late. Prof. N. K. Singh, Department of Chemistry, Banaras Hindu University.

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