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# Synthesis, spectral and structural studies of a Mn(II) complex of [N'-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid ethyl ester and Mn(II) and Ni(II) complexes of [N'-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl ester

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# ABSTRACT

The new complexes [Mn(Hpchce)<sub>2</sub>(o-phen)], {2[Mn(pchcm)(o-phen)<sub>2</sub>]}-7H<sub>2</sub>O and [Ni(Hpchcm)(ophen)<sub>2</sub>]Cl-CH<sub>3</sub>OH with [N'-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid ethyl ester (H<sub>2</sub>pchce) and [N'-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl ester (H2pchcm) have been synthesized, containing o-phenanthroline (o-phen) as a coligand. These ligands and their complexes have been characterized by elemental analyses, IR, magnetic susceptibility and single crystal X-ray data. H<sub>2</sub>pchce (2), [Mn(Hpchce)<sub>2</sub>(o-phen)] (3) {2[Mn(pchcm)(o-phen)<sub>2</sub>]}·7H<sub>2</sub>O (4) and [Ni(Hpchcm)(o-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH (5) crystallized in the monoclinic system, space group Pc, C2/c, P21/n and P21/n, respectively. The (N, O) donor sites of the bidentate ligands chelate the Mn(II) and Ni(II) centers forming a five-membered CN<sub>2</sub>OM ring. The resulting complexes are paramagnetic and have a distorted octahedral geometry.

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# 1. Introduction

Metal complexes of sulfur-nitrogen chelating ligands derived from S-alkyl esters of dithiocarbazic acid have been studied over the past two decades [1–10], not only because of their intriguing coordination chemistry, but also because of their pronounced biological activities against microbes, viruses and cancer cells [2-4]. Some Schiff bases of S-alkyl esters of dithiocarbazic acid and their complexes were found to display antifungal and antibacterial properties [5-7]. Although several papers on the syntheses and spectral characterization of metal complexes of dithiocarbazates have been reported [1-10], there is no work on the dithioester of N-acyl hydrazide, RC(O)NH-NH-C(S)SR, which also contains an NH-C=S moiety as the S-alkyl ester of dithiocarbazic acid. Following our interest in the coordination properties of ligands containing the H–N–C=S moiety and with the aim of elucidating the coordination geometry of this class of biologically important ligands, [N'-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl (H<sub>2</sub>pchcm) and ethyl (H<sub>2</sub>pchce) esters have been synthesized, and the present paper reports the syntheses, spectral characterization and X-ray crystallography of H<sub>2</sub>pchce, [Mn (Hpchce)<sub>2</sub>(o-phen)], {2[Mn(pchcm)(o-phen)<sub>2</sub>]}·7H<sub>2</sub>O and [Ni(Hp chcm)(o-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH (o-phen = o-phenanthroline).

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# 2. Experimental

# 2.1. Materials and methods

Commercial reagents were used without further purification and all experiments were carried out in the open atmosphere. Isonicotinic acid hydrazide (Sigma Aldrich), CS<sub>2</sub> (S D Fine Chemicals, India) and KOH (Qualigens) were used as received. All the solvents were purchased from Merk Chemicals, India and used after purification.

## 2.2. Preparations of $[K^+(H_2L)^-]$

The potassium N-(pyridine-4-carbonyl)-hydrazine carbodithioate  $[K^{+}(H_2L)^{-}]$  was prepared by adding CS<sub>2</sub> (1.5 ml, 20 mmol) dropwise to a suspension of isonicotinic acid hydrazide (2.7 g, 20 mmol) in methanol (30 ml) in the presence of potassium hydroxide (1.2 g, 20 mmol). The reaction mixture was stirred continuously for 30 min and the yellow solid  $[K^+(H_2L)^-]$  which separated was filtered, washed with EtOH and dried. Yield: 77%. M.p. 578 K. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>; δ ppm): 10.60 (s, 2H, NH), 8.65, 7.85 (m, 4H, pyridine ring). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>; δ ppm): 203.03 (>C=S), 163.88 (>C=O), 131.77 (C3), 150.56 (C6), 140.27 (C5), 121.01 (C4), 118.63 (C7). IR (v cm<sup>-1</sup>, KBr): v(NH) 3289m, 3182m; v(C=O) 1676s; v(N-N) 1062s; v(C=S) 993s; pyridine ring 667. Anal.



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Calc. for  $C_7H_6N_3OS_2K$  (251.36): C, 33.45; H, 2.41; N, 16.72; S, 25.51. Found: C, 33.40; H, 2.35; N, 16.76; S, 25.45%.

# 2.2.1. Synthesis of N'-(pyridine-4-carbonyl)-hydrazinecarbodithioic acid methyl ester (1)

The N'-(pyridine-4-carbonyl)-hydrazinecarbodithioic acid methyl ester (H<sub>2</sub>pchcm) was synthesized by the dropwise addition of methyl iodide (1 ml, 8 mmol) to a suspension of freshly prepared potassium [N'-(pyridine-4-carbonyl) hydrazine] carbodithioate  $[K^+(H_2L)^-]$  (2 g, 8 mmol) in methanol (15 ml), and the reaction mixture was stirred continuously for 2 h at room temperature and filtered to remove the residue. On evaporation of the solvent and acidification of the product with dilute CH<sub>3</sub>COOH (20% v/v), a 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. 443 K. Anal. Calc. for C<sub>8</sub>H<sub>9</sub>N<sub>3</sub>OS<sub>2</sub> (227.30): C, 42.27; H, 3.99; N, 18.48; S, 28. 21. Found: C. 42.20; H. 4.05; N. 18.36; S. 28.30%. IR (v cm<sup>-1</sup>, KBr); v(NH) 3241m. 3199m: v(C=O) 1691s: v(N-N) 1062s: v(C=S) 908m: pvridine ring 681: (CH<sub>3</sub>) 2926. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>:  $\delta$  ppm): 11.55. 11.75 (m, 2H, -NH), 7.8, 8.9 (4H, pyridine ring), 1.5 (s, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>;  $\delta$  ppm): 138.82 (C3), 121.36 (C4), 150.62 (C5), 150.49 (C6), 121.28 (C7), 164.04 (>C2=0), 204.11 (>C1=S), 16.92 (C8).

# 2.2.2. Synthesis of N'-(pyridine-4-carbonyl)-hydrazinecarbodithioic acid ethyl ester (**2**)

The N'-(pyridine-4-carbonyl)-hydrazinecarbodithioic acid ethyl ester (H<sub>2</sub>pchce) was synthesized by the dropwise addition of ethyl iodide (1 ml, 8 mmol) to a suspension of freshly prepared potassium [N'-(pyridine-4-carbonyl) hydrazine] carbodithioate  $[K^{+}(H_{2}L)^{-}]$  (2 g, 8 mmol) in methanol (15 ml), and the reaction mixture was stirred continuously for 2 h at room temperature. The resulting yellow solution was filtered off. On evaporation of the solvent and acidification of the residue with acetic acid (20% v/v), the solid obtained was washed twice with portions of an ethanol-water mixture (50:50) and finally dried in vacuo. Colorless needle shaped crystals of the compound suitable for X-ray analyses were obtained by slow evaporation of its methanol solution over a period of 12 days. Yield 62%. M.p. 438 K; Anal. Calc. for C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>S<sub>2</sub>O (241.33): C, 44.75; H, 4.55; N, 17.40; S 26.51. Found: C, 44.30; H, 4.62; N, 17.65; S, 26.36%. IR (cm<sup>-1</sup>, KBr): v(NH) 3281m, 3169m; v(C=O) 1688s; v(N-N) 1061; v(C=S) 909; pyridine ring 692. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>;  $\delta$  ppm): 7.8, 8.8 (m, 4H pyridine ring), 11.60 (s, 2H, NH), 1.2 (t, 3H, I = 5.4 Hz), 3.25 (g, 2H, I = 6.3 Hz). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>;  $\delta$  ppm): 203.12 (>C=S), 163.90 (>C=O), 150.88 (C1), 121.41 (C2), 150.47 (C3), 139.36 (C4), 119.65 (C5), 28.55 (C8), 14.33 (C9). MS (FAB)  $m/z = 242 \text{ [M]}^+$ . The structure was further confirmed by XRD.

#### 2.2.3. Preparation of [Mn(Hpchce)<sub>2</sub>(o-phen)] (**3**)

Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.244 g, 1 mmol) and H<sub>2</sub>pchce (**2**) (0.482 g, 2 mmol) were dissolved separately in 20 ml methanol, mixed together and stirred for 1 h. The yellow solid which separated was filtered, washed successively with an ethanol–water mixture (50:50) and air dried. A methanol solution of *o*-phen (0.20 g, 1 mmol) was added to the methanol suspension of the above compound and stirred for 3 h. The resulting clear yellow solution was filtered and kept for crystallization. Pale yellow single crystals of **3** suitable for X-ray analyses were obtained by slow evaporation of its methanol solution over a period of 14 days. Yield 58%. M.p. 489 K.  $\mu_{eff}$  = 5.9 BM. *Anal.* Calc. for C<sub>30</sub>H<sub>28</sub>MnN<sub>8</sub>O<sub>2</sub>S<sub>4</sub> (715.78): C, 50.29; H, 3.91; N, 15.64; S 17.88. Found: C, 50.10; H, 3.98; N, 15.81; S, 17.62%. IR (cm<sup>-1</sup>, KBr): *v*(NH) 3132m; *v*(C=O) 1614s; *v*(N–N) 1097; *v*(C=S) 905; pyridine ring 969, 662.

## 2.2.4. Preparation of $\{2[Mn(pchcm)(o-phen)_2]\}$ ·7H<sub>2</sub>O (4)

A solution of H<sub>2</sub>pchcm (**1**) (0.454 g, 2 mmol) in MeOH (10 ml) was added to a MeOH solution (10 ml) of Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.244 g, 1 mmol). This mixture was magnetically stirred for 3 h at room temperature. The resulting precipitate was filtered off, washed thoroughly with EtOH and air dried. This was suspended in MeOH to which *o*-phen (0.400 g, 2 mmol) was added and magnetically stirred for 2 h at room temperature. The resulting clear red solution was filtered off and kept for crystallization. Light red single crystals of **4** suitable for X-ray analysis were obtained by slow evaporation of the above methanolic solution over a period of 12 days. Yield 58%. M.p. 493 K.  $\mu_{eff}$  = 6.00 BM. *Anal.* Calc. for C<sub>64</sub>H<sub>60</sub>Mn<sub>2</sub>N<sub>14</sub>O<sub>9</sub>S<sub>4</sub> (1407.38): C, 54.62; H, 4.29; N, 13.97; S, 9.11. Found: C, 54.79; H, 4.30; N, 13.58; S, 9.10%. IR ( $\nu$  cm<sup>-1</sup>, KBr):  $\nu$ (>C=N) 1591s;  $\nu$ (N–N) 1096;  $\nu$ (>C=S) 908; pyridine ring 636; CH<sub>3</sub> 2962. The structure was further confirmed by XRD.

## 2.2.5. [Ni(Hpchcm)(o-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH (5)

NiCl<sub>2</sub>·6H<sub>2</sub>O (0.237 g, 1 mmol) and H<sub>2</sub>pchcm (1) (0.454 g, 2 mmol) were dissolved separately in 20 ml methanol, mixed together and stirred for 1 h. The brown solid which separated was filtered, washed successively with an ethanol–water mixture (50:50) and air dried. A methanol solution of *o*-phen (0.400 g, 2 mmol) was added to the methanol suspension of the above compound and stirred for 2 h. The resulting clear brown solution was filtered and kept for crystallization. Brown single crystals of **5** suitable for X-ray analyses were obtained by slow evaporation of its methanol solution over a period of 10 days. Yield 60%. M.p. 503 K.  $\mu_{eff}$  = 2.87 BM. *Anal.* Calc. for C<sub>33</sub>H<sub>28</sub>ClN<sub>7</sub>NiO<sub>2</sub>S<sub>2</sub> (712.90): C, 55.54; H, 3.92; N, 13.74; S, 8.97. Found: C, 55.55; H, 3.90; N, 13.75; S, 8.96%. IR ( $\nu$  cm<sup>-1</sup>, KBr):  $\nu$ (OH) 3427;  $\nu$ (NH) 3169;  $\nu$ (>C=O) 1676s;  $\nu$ (N–N) 1062;  $\nu$ (>C=S) 993. The structure was further confirmed by XRD.



Fig. 1a. ORTEP diagram of H<sub>2</sub>pchce (2) with ellipsoids at the 30% probability level. H atoms are omitted for clarity.



Fig. 1b. Packing diagram of H<sub>2</sub>pchce (2) along the b axis.

#### 2.3. Physical measurements

Carbon, hydrogen and nitrogen contents were estimated on a Carlo Erba 1108 model microanalyser. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using Hg[Co(NCS)<sub>4</sub>] as the calibrant. Electronic spectra were recorded on a CARY 100 Varian EL 01055314 UV– Vis spectrophotometer in MeOH. IR spectra were recorded in the 4000–400 cm<sup>-1</sup> region as KBr pellets on a Varian 3100-FT IR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in DMSO-d<sub>6</sub> on a JEOL AL 300 FT NMR spectrometer using TMS as an internal reference. The FAB mass spectra were recorded on a Jeol SX 102/ Da-600 mass spectrometer/data system using Argon/Xenon (6 kV, 10 m A0) as the FAB gas and *m*-nitro benzyl alcohol (NBA) as the matrix.

#### 3. Crystal structure determination

Data for the structures of **2** and **5** were obtained at 173(2) and 296(2) K, respectively on a Bruker three-circle diffractometer equipped with SMART 6000 CCD software whereas those of 3 and 4 were obtained at 293(2) and 150(2) K, respectively on an Oxford Diffraction Gemini diffractometer equipped with CrysAlis Pro., using a graphite mono-chromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation source. The structures were solved by direct methods (SHELXL-97) and refined against all data by full matrix least-squares on F<sup>2</sup> using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the refinement at geometrically ideal positions and were refined with a riding model [11,12]. The MERCURY package and ORTEP-3 for Windows program were used for generating the structures [13,14]. In the case of H<sub>2</sub>pchce, having two molecules in the asymmetric unit, the ethyl group of one molecule is disordered but the overall structure is unambiguous.

# 4. Results and discussion

The ligands [N'-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl (H<sub>2</sub>pchcm) and ethyl (H<sub>2</sub>pchce) esters react with  $Mn(OAc)_2$ ·4H<sub>2</sub>O to form yellow and red precipitates, respectively, which dissolve in methanolic solutions of *o*-phen yielding [Mn(H<sub>2</sub>pchce)<sub>2</sub>(*o*-phen)] (**3**) and {2[Mn(pchcm)(*o*-phen)<sub>2</sub>]}·7H<sub>2</sub>O (**4**). [N'-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl ester (H<sub>2</sub>pchcm) reacts with NiCl<sub>2</sub>·6H<sub>2</sub>O and *o*-phen to yield [Ni(Hpchcm)(*o*-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH (**5**). These complexes are stable towards air and moisture. Scheme 1 depicts the formation of the complexes which contain [pchcm]<sup>2–</sup> and [Hpchce]<sup>–</sup> as ligands and *o*-phen as the coligand. The ligands **1** and **2** are soluble in methanol and ethanol while compounds **3**, **4** and **5** dissolve in

DMF and DMSO. The ligands **1** and **2** and the complexes **3**, **4** and **5** melt at 443, 438, 489, 493 and 503 K, respectively.

#### 4.1. IR spectra

The IR spectra of the ligands N'-(pyridine-4-carbonyl)-hydrazinecarbodithioic acid esters (1) and (2) show absorptions due to the stretching modes of NH (3241–3281, 3199–3169 cm<sup>-1</sup>), C=O (1691-1688 cm<sup>-1</sup>), C=S (908-909 cm<sup>-1</sup>) and N-N (1061- $1062 \text{ cm}^{-1}$ ). The IR spectrum of complex **3** shows a band at 3132 cm<sup>-1</sup>, indicating the presence of one NH group upon complexation. The appearance of two new bands for v(Mn-N) at 441 and 497 cm<sup>-1</sup> suggests bonding of Mn(II) with o-phen and one hydrazinic nitrogen after loss of a proton. The v(C=0) and v(N-N) bands suffer negative and positive shifts of 74 and 36  $cm^{-1}$ , respectively, indicating that H<sub>2</sub>pchce is acting as a uninegative bidentate ligand, bonding through the carbonyl oxygen and hydrazinic nitrogen atoms in complex 3. In complex 4, the absence of v(N-H) bands at 3241 and 3199 cm<sup>-1</sup> shows the loss of both hydrazinic protons, and the appearance of a new band due to  $v(C=N \text{ of } NCO) \text{ at } 1591 \text{ cm}^{-1} \text{ in place of } v(C=O), \text{ suggests bonding}$ through the enolic oxygen and one hydrazinic nitrogen atom. Furthermore, the appearance of two new bands due to v(Mn–N) at 436 and 452 cm<sup>-1</sup> and a positive shift of 34 cm<sup>-1</sup> in v(N–N) suggest bonding of Mn(II) with the *o*-phen nitrogen and one hydrazinic nitrogen atom. The IR spectrum of [Ni(Hpchcm)(o-phen)2]Cl- $CH_3OH$  (**5**) shows two bands at 3427 and 3169 cm<sup>-1</sup> for v(OH) of CH<sub>3</sub>OH and v(NH). The absence of one v(NH) band together with the appearance of a new band for v(Ni-N) at 474 cm<sup>-1</sup> suggests bonding of Ni(II) with one hydrazinic nitrogen atom after the loss of a proton. The v(C=0) and v(N-N) bands suffer negative and positive shifts, indicating bonding through the carbonyl oxygen and one hydrazinic nitrogen atom. Thus, H<sub>2</sub>pchcm acts as an uninegative bidentate ligand in complex 5 and as dinegative bidentate ligand in complex **4**, bonding through the carbonyl/enolic oxygen and one hydrazinic nitrogen atom [15].

# 4.2. <sup>1</sup>H and <sup>13</sup>C NMR spectra

The <sup>1</sup>H NMR spectrum of H<sub>2</sub>pchcm (**1**) exhibits two signals at  $\delta$  11.75 and 11.55 ppm for the amide and thioamide protons, respectively, and one signal at 1.5 ppm due to methyl protons. Four protons of the pyridine ring appear as a multiplet between  $\delta$  7.8–8.9 ppm. The <sup>13</sup>C NMR spectrum of **1** shows 8 signals for eight carbon atoms, of which the signals at  $\delta$  204.11 and 164.04 ppm are due to the >C=S and >C=O, carbons, respectively. The signal for the >CH<sub>3</sub> carbons are observed at  $\delta$  16.92 ppm. The pyridine ring carbons appear at C3: 138.82, C4: 121.36, C5: 150.62, C6: 150.49 and C7: 121.28 ppm. The <sup>1</sup>H NMR spectrum



Scheme 1. Preparation of the ligands and the complexes.

of  $\rm H_2pchce$  in DMSO-d\_6 shows signals at  $\delta$  11.60 (s, 2H), 1.2 (t, 3H, J = 5.4 Hz) and 3.25 (q, 2H, J = 6.3 Hz) ppm due to NH, CH<sub>3</sub> and CH<sub>2</sub> protons, respectively. The pyridine ring protons appear

as a multiplet between 7.8 and 8.8 (m, 4H) ppm. The  $^{13}\mathrm{C}$  NMR spectrum of H<sub>2</sub>pchce shows signals at  $\delta$  203.12, 163.90, 28.55 and 14.33 ppm due to >(C=S), >(C=O), >CH<sub>2</sub> and >CH<sub>3</sub> carbons,

Table 1

Crystallographic data for H2pchce (2), [Mn(Hpchce)2 (o-phen)] (3), {2[Mn((pchcm) (o-phen)2]]-7H2O (4) and [Ni(Hpchcm) (o-phen)2]Cl-CH3OH (5).

Compound	2	3	4	5
	-		-	
Empirical formula	$C_9H_{11}N_3OS_2$	$C_{30}H_{28}MnN_8O_2S_4$	$C_{64}H_{60}Mn_2N_{14}O_9S_4$	$C_{33}H_{28}CIN_7N_1O_2S_2$
Formula weight	241.33	715.78	1407.38	712.90
T (K)	173(2)	293(2)	150(2)	296(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	Pc	C2/c	P21/n	P21/n
a (Å)	9.690(3)	18.066(6)	16.671(3)	16.6963(14)
b (Å)	9.125(2)	11.211(3)	11.0491(17)	10.8245(10)
c (Å)	13.420(3)	17.262(2)	19.045 (4)	19.0139(17)
β(°)	97.658	109.266(19)	114.01(2)	113.430(3)
$V(Å^3)$	1176.1(5)	3300.4(14)	3204.7(10)	3153.0(5)
Ζ	4	4	2	4
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.363	1.441	1.460	1.502
$\mu ({\rm mm}^{-1})$	0.430	0.695	0.595	0.877
$F(0 \ 0 \ 0)$	504	1476	1444	1472
Crystal size (mm)	0.66  imes 0.41  imes 0.29	0.33  imes 0.26  imes 0.21	0.33  imes 0.28  imes 0.25	$0.20\times0.18\times0.17$
$\theta$ Range for data collection (°)	2.12-29.47	3.00-25.00	3.06-32.62	1.38-28.30
Index ranges	$-13 \le h \le 10, -12 \le k \le 11,$	$-21 \le h \le 21, -13 \le k \le 13.$	$-24 \le h \le 25, -15 \le k \le 16.$	$-18 \le h \le 22, -14 \le k \le 12.$
	$-18 \leq l \leq 18$	$-20 \le l \le 20$	$-27 \leq l \leq 28$	$-25 \leq l \leq 24$
Number of reflections collected	8479	14 342	38 509	7839
Number of independent	5100(0.0243)	2907(0.0463)	10 618(0.1814)	4546(0.0632)
reflections( $R_{int}$ )				
Number of data/restraints/	5100/15/290	2907/0/208	10 618/0/425	7839/0/408
parameters				
Goodness-of-fit (GOF) on F <sup>2</sup>	1.062	1.111	0.756	1.509
$R_1, w R_2^{a,b} [(I > 2\sigma(I))]$	0.0518, 0.1248	0.0470, 0.1195	0.0492, 0.0800	0.1342, 0.2473
$R_1$ , $wR_2^{a,b}$ (all data)	0.0676, 0.1334	0.0677, 0.1334	0.2416, 0.0999	0.0697, 0.2473
Largest difference in peak and	0.574 and -0.416	0.808 and -0.547	0.619 and -0.395	0.265 and -0.877
hole (e Å <sup>-3</sup> )				

 $\label{eq:rescaled_rescale$ 

Table 2		
Selected bond length	s (Å) and angles	(°) for H <sub>2</sub> pchce (2).

Bond lengths			
S(1A)-C(7A)	1.743(4)	S(1BA)-C(7B)	1.778(4)
S(1A)-C(8A)	1.812(18)	S(1BB)-C(8BB)	1.811(19)
S(2A)-C(7A)	1.662(3)	S(2BA)-C(7B)	1.672(5)
O(1A)-C(6A)	1.219(4)	O(1B)-C(6B)	1.217(4)
N(2A)-C(6A)	1.346(4)	N(2B)-C(6B)	1.335(4)
N(2A)-N(3A)	1.394(3)	N(2B)-N(3B)	1.385(3)
N(3A)-C(7A)	1.331(4)	N(3B)-C(7B)	1.341(4)
C(1A)-C(6A)	1.496(4)	C(1B)-C(6B)	1.505(4)
C(8A)-C(9A)	1.468(19)	C(8BA)-C(9BA)	1.468(19)
Bond angles			
C(7A)-S(1A)-C(8A)	102.5(18)	C(7B)-S(1BB)-C(8BB)	105.3(4)
C(6A)-N(2A)-N(3A)	118.4(2)	C(8BB)-S(1BB)-C(9BB)	112.2(17)
C(7A)-N(3A)-N(2A)	122.3(3)	C(6B)-N(2B)-N(3B)	119.2(2)
O(1A)-C(6A)-N(2A)	121.8(3)	C(7B)-N(3B)-N(2B)	120.2(3)
O(1A)-C(6A)-C(1A)	121.7(3)	O(1B)-C(6B)-N(2B)	122.6(3)
N(2A)-C(6A)-C(1A)	116.3(3)	O(1B)-C(6B)-C(1B)	121.8(3)
N(3A)-C(7A)-S(2A)	119.2(3)	N(2B)-C(6B)-C(1B)	115.6(3)
N(3A)-C(7A)-S(1A)	113.5(2)	N(3B)-C(7B)-S(2BB)	128.7(3)
S(2A)-C(7A)-S(1A)	127.2(2)	N(3B)-C(7B)-S(1BA)	108.0(2)
C(9A)-C(8A)-S(1A)	112.3(16)	S(2BA)-C(7B)-S(1BA)	126.7(3)
		C(9BA)-C(8BA)-S(1BB)	112.4(16)

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Hydrogen bonds for  $H_2$  pchce [Å and °] (2).

D-H…A	<i>d</i> (D–H)	<i>d</i> (H…A)	<i>d</i> (D…A)	∠(DHA)
$\begin{array}{l} N(2A)H(2AB)\cdots O(1B)\#1\\ N(3A)H(3AB)\cdots N(1A)\#2\\ N(2B)-H(2BB)\cdots O(1A)\\ N(3B)H(3BB)\cdots N(1B)\#3 \end{array}$	0.88	1.93	2.754(4)	155.1
	0.88	2.06	2.850(4)	149.3
	0.88	1.95	2.744(4)	149.8
	0.88	2.01	2.793(4)	148.0

#1 x - 1, y, z; #2 x, -y + 3, z - 1/2; #3 x, -y + 2, z - 1/2.

respectively. The pyridine ring carbons appear at C1: 150.88, C2: 121.41, C3: 150.47, C4: 139.36 and C5: 119.65 ppm [16].

#### 4.3. Mass spectrometry

The ligand  $H_2$  pchce is identified by its FAB mass spectrum which shows many peaks due to various fragments. A peak at m/

*z* = 242 corresponds to  $[M+H]^+$ . Other important peaks at *m*/ *z* = 208 (29% intensity), 180 (91%) and 136 (48%) correspond to the fragments formed from  $[M+H]^+$  after release of H<sub>2</sub>S (34), HSC<sub>2</sub>H<sub>5</sub> (62) and HCS<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (105), respectively.

#### 4.4. Electronic spectra and magnetic moments

[Mn(Hpchce)<sub>2</sub>(*o*-phen)] (**3**) shows a magnetic moment of 5.9 BM which indicates the presence of five unpaired electrons. It shows one low intensity absorption at 15 220 cm<sup>-1</sup> assigned to the  ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$  transition, characteristic of a distorted octahedral Mn(II) complex. The other two bands observed at 28 170 and 38 160 cm<sup>-1</sup> may be assigned to intraligand/charge transfer transitions [17]. The magnetic moment of 6.00 BM for {2[Mn(pchcm) (*o*-phen)<sub>2</sub>]}·7H<sub>2</sub>O (**4**) suggests a high spin Mn(II) center with five unpaired electrons. Its electronic spectrum shows a band at 25 510 cm<sup>-1</sup>, which may be assigned to a charge transfer transition. A magnetic moment of 2.87 BM for [Ni(Hpchcm)(*o*-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH (**5**) and the presence of a band at 17 200 cm<sup>-1</sup>, assigned to the  ${}^{3}A_{2g} \rightarrow {}^{3}A_{1g}(F)$  transition, suggests a distorted octahedral geometry for the complex.

#### 4.5. Crystal structure description of $H_2$ pchce (2)

The crystallographic data and structural refinement details are given in Table 1 and selected bond distances and bond angles are given in Table 2. Hydrogen bonding parameters of the ligand are given in Table 3. Fig. 1a shows the ORTEP diagram of the H<sub>2</sub>pchce (**2**) ligand with the atomic numbering scheme and Fig. 1b shows the packing diagram of the ligand along the *b* axis. The structure of H<sub>2</sub>pchce is stabilized by intermolecular N–H···N and N–H···O hydrogen bonding, responsible for producing a three dimensional structure (Fig. 1b). In addition to this, there is a C–H···O weak interaction between the carbonyl oxygen and pyridine ring hydrogen at position 3. The distances and angles for H<sub>2</sub>pchce are close to those reported earlier [18,19]. The N–H···N hydrogen bonds are formed between the pyridine nitrogen and hydrazinic hydrogen, and N–H···O hydrogen bonds are formed between the hydrazinic hydrogen and carbonyl oxygen.



Fig. 2. ORTEP diagram of the Mn(II) complex 3 with ellipsoids at the 30% probability level. H atoms are omitted for clarity.

The C–S bond distances of 1.743(4) and 1.662(3) Å (Table 2) in H<sub>2</sub>pchce agree well with those in related compounds, being intermediate between 1.82 Å for a C–S single bond and 1.56 Å for a C–S double bond [20].

## 4.6. Crystal structure description of $[Mn(Hpchce)_2 (o-phen)]$ (3)

Fig. 2 shows the ORTEP diagram of complex 3 with the atomic numbering scheme. The structural refinement data related to complex **3** are listed in Table 1 and selected bond distances and bond angles are listed in Table 4. The metal center in complex **3** is coordinated in a N4O2 core by two uninegative bidentate ligands using hydrazine nitrogen (N1, after loss of a proton) and carbonyl oxygen atoms. The manganese atom in complex 3 is located on a twofold axis which passes through the middle of the C15-C15' bond. The distances found within the chelate rings are intermediate between single and double bond lengths and are also longer or shorter than the corresponding bond lengths in  $H_2$  pchce (2). The average bond lengths in complex 3 are: 01– C6 = 1.241(4) (L), N2-C6 = 1.322(4) (S), N2-N3 = 1.391(4) (S), N3–C7 = 1.329(4) (S) Å (L = longer, S = shorter), and these suggest considerable delocalization of charge [21]. The (N, O) donor sites of the bidentate ligand chelates the Mn(II) center to form a fivemembered CN<sub>2</sub>OMn ring. The resulting complex has a distorted octahedral geometry. The Mn-O bond length in (3) is 2.173 Å and the Mn-N bond lengths are 2.257 and 2.270 Å for Mn-N (hydrazinic) and Mn-N (o-phen), respectively. The shorter Mn-N (hydrazinic) bond length as compared to Mn-N (o-phen) indicates that the hydrazinic nitrogen bonds more strongly than the o-phen nitrogen. The bond angles N(4)-Mn-N(3) 162.83(9)° and N(4)-Mn-N(4) 73.70(13)° indicate distortion from an ideal octahedral geometry [22]. In the complex **3** the C(7)–N(3) and C(6)– N(2) bond distances show partial double bond character due to delocalization of  $\pi$  electrons throughout the whole chelate ring [23]. Both metal chelate rings present in complex 3 exhibit some degree of metalloaromaticity [24,25]. Both chelate rings around Mn(II) formed by (Hpchce)<sup>–</sup> are almost orthogonal to each other, forming a dihedral angle of 88.62°. In the complex the chelate rings and the pyridine rings lie nearly in the same plane, forming a dihedral angle of 14.44°. Due to the deprotonation of the hydrazinic hydrogen, the intermolecular hydrogen bonding present between the pyridine nitrogen and hydrazinic hydrogen in the ligand of 2 disappears in complex 3. The N-H-O intermolecular hydrogen bonding is also absent due to involvement of the

Table	4
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Selected bond lengths (Å) a	and angles (°) for [Mn((Hpchce) <sub>2</sub> (o-phen)] (3)

Bond lengths			
Mn1-01	2.173(2)	N2-N3	1.391(4)
Mn1-N4	2.257(3)	N3-C7	1.329(4)
Mn1-N3	2.270(3)	N4-C10	1.328(4)
S1-C7	1.685(3)	N4-C14	1.352(4)
S2-C7	1.768(4)	01-C6	1.241(4)
N2-C6	1.322(4)	C8-C9	1.453(7)
Bond angles			
01-Mn1-01	176.01(12)	C7-N3-Mn1	138.2(2)
01-Mn1-N4	92.51(8)	N2-N3-Mn1	108.23(19)
01-Mn1-N4	90.68(9)	C10-N4-Mn1	126.6(2)
N4-Mn1-N4	73.70(13)	C14-N4-Mn1	115.29(20)
01-Mn1-N3	73.53(9)	C6-O1-Mn1	116.0(2)
01-Mn1-N3	103.73(9)	01-C6-N2	121.7(3)
N4-Mn1-N3	162.83(9)	01-C6-C5	120.8(3)
N4-Mn1-N3	96.07(10)	N2-C6-C5	117.5(3)
N3-Mn1-N3	96.93(14)	N3-C7-S1	126.2(3)
C7-S2-C8	106.0(2)	N3-C7-S2	109.8(2)
C6-N2-N3	119.3(3)	S1-C7-S2	123.9(2)
C7-N3-N2	113.1(3)	C9-C8-S2	113.6(4)

carbonyl oxygen in coordination with Mn(II). Compound **3** is quite stable in the solid state due to  $\pi$  electron delocalization and weak intermolecular C–H…S interactions between the thioe-ther sulfur of one molecule and a methyl hydrogen atom of a nearby molecule. The crystal structure in turn is stabilized by intramolecular and intermolecular hydrogen bonding.

# 4.7. Crystal structure description of {2[Mn(pchcm)(o-phen)<sub>2</sub>]}·7H<sub>2</sub>O (**4**)

Fig. 3a shows an ORTEP diagram of complex **4** together with the atom numbering scheme. The structural refinement data related to complex **4** are listed in Table 1 and selected bond distances and bond angles are listed in Table 5. For complex **4**, the multiplicities of O1W, O2W and O4W refined to values close to 1 while for O3W the value refined too close to 0.5. Therefore O3W is in partial occupancy. The (N, O) donor sites of the dinegative bidentate ligand chelate the Mn(II) center to form a five-membered CN<sub>2</sub>OMn ring. The average bond lengths in complex **4** are: O1–C2 = 1.301(12)



Fig. 3a. ORTEP diagram of compound 4. Hydrogen atoms and solvent molecules are not shown.

Table 5

Selected bond lengths (Å) and angles (°) for {2[Mn((pchcm)(o-phen)<sub>2</sub>]}·7H<sub>2</sub>O (4).

	0 () 0 ()		,21) 2 ( )
Bond lengths			
Mn1-01	2.152(7)	S2-C32	1.794(11)
Mn1-N1	2.169(9)	01-C2	1.301(12)
Mn1-N4	2.247(10)	N1-C1	1.293(11)
Mn1-N6	2.275(8)	N1-N2	1.414(11)
Mn1-N7	2.289(10)	N2-C2	1.309(12)
Mn1-N5	2.292(9)	N3-C6	1.336(14)
S1-C1	1.711(10)	N3-C5	1.342(16)
S2-C1	1.801(11)	N4-C8	1.313(13)
Bond angles			
01-Mn1-N1	73.67(3)	C2-01-Mn1	111.77(6)
01-Mn1-N4	101.68(3)	C1-N1-N2	114.61(8)
N1-Mn1-N4	104.51(3)	C1-N1-Mn1	129.94(7)
N1-Mn1-N6	109.47(3)	N2-N1-Mn	114.54(5)
N4-Mn1-N6	92.87(3)	C2-N2-N1	110.52(8)
01-Mn1-N7	91.30(3)	C6-N3-C5	115.77(9)
N1-Mn1-N7	96.49(4)	C19-N4-Mn1	116.09(7)
N4-Mn1-N7	157.68(3)	C17-N5-Mn1	127.85(9)
N6-Mn1-N7	72.77(3)	C18-N5-Mn1	114.83(6)
01-Mn1-N5	88.72(3)	N1-C1-S1	121.28(8)
N1-Mn1-N5	161.58(3)	N1-C1-S2	117.48(8)
N4-Mn1-N5	73.27(3)	S1-C1-S2	121.24(5)
N6-Mn1-N5	88.96(3)	01-C2-N2	126.33(9)
N7-Mn1-N5	89.13(4)	01-C2-C3	117.83(8)
C1-S2-C32	103.21(5)	N2-C2-C3	115.83(9)



Fig. 3b. Triangular arrangement of the three water molecules in the crystal structure of complex 4.



Fig. 4. Ortep diagram of compound 5. Hydrogen atoms and solvent molecules are not shown.

(L), N2-C2 = 1.309(12) (S), N1-N2 = 1.414(11) (L), N1-C1 = 1.293(11)(S)Å (L = longer, S = shorter), which suggest considerable delocalization of charge [23]. A large increase in the C-O bond length as compared to complex **3** suggests a change of C=O double bond to C-O single bond on account of enolization and the subsequent release of a proton for the formation of a chelate ring with Mn(II). The resulting complex has a distorted octahedral geometry. Masui suggested that if active electron delocalization within a metal-N-heterocyclic chelate ring is present, it would exhibit some degree of metalloaromaticity [24,25]. In the complex the chelate rings and the pyridine rings lie nearly in the same plane, forming a dihedral angle of 19.97°. The bond distances for Mn-O, Mn-N and Mn-N(phen) are 2.152(7), 2.179(9) and 2.275(8) Å, respectively, which are comparable to the bond lengths reported for  $[Mn_3(O_2CCH_3)_6(N-N)_2]$  (where N-N = 0-phen) [26] and  $[Mn_2(phen)(Hdcbi)]_n$  (Hdcbi = 4,5-dicarboxyimidazole) [27].

Three of the four water molecules present in the lattice form a triangular structure out of which one water molecule links the complex through O–H…S and another by O–H…O (carbonyl) intermolecular hydrogen bonding to form a supramolecular arrangement (Fig. 3b). The fourth water molecule is linked to the pyridine nitrogen of one unit and a CH<sub>3</sub> hydrogen of another unit.

# 4.8. Crystal structure description of [Ni (Hpchcm) (o-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH (**5**)

Fig. 4 shows the ORTEP diagram of complex **5** together with the atom numbering scheme. The structural refinement data related to complex **5** are listed in Table 1 and selected bond distances and bond angles are listed in Table 6. In compound **5**, the chlorine atom (Cl1) and the atoms of methanol (C33 and O2) were found to be disordered over two positions with occupancies of 0.57:0.43,

Table 6
Selected bond lengths (Å) and angles (°) for [Ni(Hpchcm)(o-phen) <sub>2</sub> ]Cl·CH <sub>3</sub> OH.

Bond lengths			
Ni1-01	2.037(3)	S2-C25	1.805(5)
Ni1-N5	2.094(4)	01-C27	1.300(5)
Ni1-N3	2.081(4)	N5-C26	1.312(5)
Ni1-N1	2.108(4)	N6-C27	1.297(5)
Ni1-N2	2.112(4)	N6-N5	1.405(5)
Ni1-N4	2.118(4)	N7-C30	1.337(7)
S1-C26	1.690(5)	N7-C31	1.304(7)
S2-C26	1.799(5)	C33-O2	1.407(15)
Bond angles			
01-Ni1-N1	170.76(14)	N2-Ni1-N4	91.50(14)
01-Ni1-N5	78.39(13)	C26-S2-C25	103.7(3)
01-Ni1-N3	95.83(14)	C27-O1-Ni1	109.3(3)
01-Ni1-N2	92.21(14)	C26-N5-N6	114.1(4)
01-Ni1-N4	89.23.(13)	C26-N5-Ni1	135.9(3)
N3-Ni1-N5	98.32(14)	N6-N5-Ni1	109.6(2)
N3-Ni1-N1	93.39(14)	C27-N6-N5	112.9(3)
N3-Ni1-N2	167.78(15)	N5-C26-S1	123.6(4)
N5-Ni1-N2	92.29(14)	N5-C26-S2	115.0(3)
N1-Ni1-N2	78.58(15)	S1-C26-S2	121.4(2)
N3-Ni1-N4	79.46(14)	01-C27-C28	118.3(4)
N5-Ni1-N4	167.8(14)	N6-C27-O1	125.6(4)
N1-Ni1-N4	91.82(14)	N6-C27-C28	116.0(4)

0.95:0.05 and 0.41:0.59, respectively. The (N, O) donor sites of the uninegative bidentate ligand chelate the Ni(II) center to form a five-membered CN<sub>2</sub>ONi ring. The resulting complex has a distorted octahedral geometry. The average bond lengths in complex **5** are: O1–C27 = 1.300(5), N6–C27 = 1.297(5), N5–N6 = 1.405(5), N5–C26 = 1.312(5) Å, which suggest considerable delocalization of charge [23]. Complex **5** is stable in the solid state due to  $\pi$  electron delocalization and weak intermolecular C–H…Cl interactions between CH<sub>3</sub> and the phenyl ring hydrogens as well as by O–H…O interactions between the OH of methanol and the carbonyl oxygen from the chelate ring.

#### 5. Conclusions

Two new ligands [N'-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl (H<sub>2</sub>pchcm) (**1**) and ethyl (H<sub>2</sub>pchce) (**2**) esters and their [Mn(Hpchce)<sub>2</sub>(*o*-phen)] (**3**), {2[Mn(pchcm)(*o*-phen)<sub>2</sub>]}-7H<sub>2</sub>O (**4**) and [Ni(Hpchcm)(*o*-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH (**5**) complexes have been synthesized. The crystal structure of complex **3** is stabilized through weak intermolecular C-H···S interactions between the thioether sulfur of one molecule and a methyl hydrogen atom of a nearby molecule. The crystals of **3**, **4** and **5** are stabilized by intermolecular and intramolecular hydrogen bonding.

## 6. Supplementary data

CCDC 682361, 682360, 715927 and 737839 contain the supplementary crystallographic data for  $H_2$  pchce (**2**),  $[Mn(Hpchce)_2 (o-phen)]$  (**3**) {2[ $Mn((pchcm)(o-phen)_2$ ]}·7H<sub>2</sub>O (**4**) and [Ni(Hpchcm)(o-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH (**5**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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