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# Nickel(II) complexes of N(4)-substituted thiosemicarbazones derived from pyridine-2-carbaldehyde: Crystal structures, spectral aspects and Hirshfeld surface analysis



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# ABSTRACT

Seven Ni(II) complexes {[NiL<sup>1</sup><sub>2</sub>]-2H<sub>2</sub>O (**1**), [Ni<sub>2</sub>L<sup>2</sup><sub>2</sub>SO<sub>4</sub>]-1½H<sub>2</sub>O (**2**), [Ni(HL<sup>2</sup>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O-EtOH (**3**), [NiL<sup>2</sup>(HL<sup>2</sup>)]OAc·3H<sub>2</sub>O (**4**), [Ni(HL<sup>2</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (**5**), [NiL<sup>3</sup>OAC]-2½H<sub>2</sub>O (**6**), [NiL<sup>3</sup>NO<sub>3</sub>]·3H<sub>2</sub>O (**7**)} of three thiosemicarbazone ligands, *viz*pyridine-2-carbaldehyde-N(4)-*p*-methoxyphenyl thiosemicarbazone (HL<sup>1</sup>), pyridine-2-carbaldehyde-N(4)-phenethyl thiosemicarbazone (HL<sup>2</sup>) and pyridine-2-carbaldehyde-N(4)-pyridyl thiosemicarbazone [HL<sup>3</sup>] were synthesized and physico-chemically characterized by means of partial elemental analyses, molar conductivity measurements, electronic, infrared spectral studies and magnetic susceptibility measurements. In the complexes, the thiosemicarbazones coordinate both in the thione form and in the deprotonated thiolate form. Pyridine nitrogen, azomethine nitrogen and thiolate/thione sulfur are involved in coordination in all the complexes. The single crystal X-ray structures of complexes **1a**, **5** and [NiL<sup>3</sup><sub>2</sub>]·H<sub>2</sub>O (**7a**) are discussed, show octahedral coordination around Ni(II). Structural studies corroborate spectral characterization. Supramolecular interactions of the three complexes are verified by Hirshfeld surface analyses, which reveal the dominant role of van der Waals forces (H…H interactions) and confirm the reinforcement of  $\pi$ - $\pi$ /C-H… $\pi$  interactions in the crystal lattice packing of these complexes.

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## 1. Introduction

Thiosemicarbazones are considered as an important class of N, S-donor ligands due to their structural diversity and variable donor properties over a span of time [1]. The potentially beneficial biological effects such as antitumor, antibacterial, antiviral and antimalarial activities of thiosemicarbazones have added their chemistry very much interesting [2-4]. Introducing heterocyclic systems have aroused considerable interest both in the coordination chemistry and in the biological activity of thiosemicarbazones. Chelation of a thiosemicarbazone with a transition metal has become a tool for enhancing their biological activity. They can coordinate as neutral keto form or as anionic enolate form after deprotonation and can adopt a variety of different coordination modes depending on the substituents and metal ions [5]. Thiosemicarbazones contain-

ing a pyridine ring act as NNS tridentate systems. The ability to exist as E and Z stereoisomers also make these systems versatile in coordination [6]. Ni(II) thiosemicarbazone complexes have recently been reported as efficient electrocatalyst [7] and photo-induced molecular catalyst [8] for hydrogen production. Conversely the substituted derivatives of pyridine-2-carbaldehyde thiosemicarbazone (HL) and their complexes with different metal ions have drawn special attention due to their interaction with enzymes such as ribonucleotide reductases, DNA polymerase and cell thiols [9]. Some reports show that labile four-coordinated nickel(II) complexes with tridentate thiosemicarbazone ligands exhibit antibacterial activities, whereas, six-coordinated nickel(II) complexes with thiosemicarbazone ligands show no activities against the test microorganisms [10]. Based on the continuing interest of Ni(II) thiosemicarbazones, we report here seven new Ni(II) complexes of three different thiosemicarbazone ligands. The ligands include pyridine-2-carbaldehyde-N(4)-*p*-methoxyphenyl thiosemicarbazone (HL<sup>1</sup>), pyridine-2-carbaldehyde-N(4)-phenethyl thiosemicarbazone (HL<sup>2</sup>) and pyridine-2-carbaldehyde-N(4)-pyridyl thiosemicarbazone (HL<sup>3</sup>) (Scheme 1). The ligands  $HL^1$ ,  $HL^2$  and their copper(II), man-

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Scheme 1. The thiosemicarbazones HL<sup>1</sup>, HL<sup>2</sup> and HL<sup>3</sup>.

ganese(II) and cobalt(III) complexes have been reported earlier [11-13]. The spectral aspects of all the complexes are investigated and X-ray diffraction study of two of them are presented along with crystal structure of an octahedral complex, derived from a square planar complex on crystallization. Hirshfeld surface analyses of three nickel(II) complexes of three different ligands are also studied.

#### 2. Experimental

#### 2.1. Materials

Pyridine-2-carbaldehyde (Aldrich), 2-phenylethylamine, panisidine and 2-aminopyridine (Fluka) were used as received. 4-Methyl-4-phenyl-3-thiosemicarbazide was prepared as reported previously [14]. Nickel(II) nitrate hexahydrate, nickel(II) sulphate heptahydrate, nickel(II) acetate tetrahydrate, and nickel(II) perchlorate hexahydrate (Merck) were used as supplied and solvents were purified by standard procedures before use. **Caution!** Perchlorate complexes of metals with organic ligands are potentially explosive and should be handled with care.

#### 2.2. Syntheses and characterization of thiosemicarbazones

The syntheses of  $HL^1$  and  $HL^2$  and crystal structure of  $HL^2$  have been reported earlier [13,15].

#### 2.2.1. Synthesis of HL<sup>3</sup>

To a solution of 1.00 g (5. 52 mmol) of 4-methyl-4-phenyl-3thiosemicarbazide in MeCN (5 ml), was added 0.520 g (5.52 mmol) of 2-aminopyridine and 0.591 g (5.52 mmol) of pyridine-2carbaldehyde and heated at reflux for 1.5 h. The solution was chilled (overnight) by keeping in a refrigerator and the compound formed was collected by filtration through quantitative filter paper, washed well with MeCN (10 ml) and recrystallized from ethanol (80 ml). It was then dried *in vacuo* over  $P_4O_{10}$ . Yield 52%, M.P. 176–177 °C. Elemental Anal. Found (Calc.): C, 55.72 (56.01); H, 4.40 (4.31); N, 27.75 (27.22); S, 12.18 (12.46)%.

#### 2.3. Syntheses of complexes

2.3.1. Syntheses of  $[NiL_2] \cdot 2H_2O$  (**1**),  $[Ni(HL_2)_2](NO_3)_2 \cdot H_2O \cdot EtOH$  (**3**),  $[NiL_3NO_3] \cdot 3H_2O$  (**7**)

To a solution of the respective ligand (1 mmol) in 25 ml hot boiling ethanol at 82 °C was added Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1 mmol) and heated under reflux at 84 °C for two hours and the resulting solution was kept to cool down naturally at room temperature overnight. The complexes formed were filtered, washed thoroughly with 5 ml each of water, ethanol and ether and dried *in vacuo* over  $P_4O_{10}$ .

## 2.3.2. Synthesis of $[Ni_2L^2_2SO_4] \cdot 1\frac{1}{2}H_2O(2)$

To a solution of the  $HL^2$  (1 mmol) in 25 ml hot boiling ethanol at 82 °C was added a solution of NiSO<sub>4</sub>·7H<sub>2</sub>O (1 mmol) in a mixture of ethanol (15 ml) and water (10 ml) and heated under reflux at 84 °C for four hours and the resulting solution was kept to cool down naturally at room temperature overnight. The complex formed was filtered, washed thoroughly with 5 ml each of water, ethanol and ether and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

# 2.3.3. Syntheses of $[Ni(L^2)(HL^2)](OAc)\cdot 3H_2O$ (4) and $[NiL^3(OAc)]\cdot 2\frac{1}{2}H_2O$ (6)

To a solution of the respective ligand (1 mmol)) in 25 ml hot boiling ethanol at 82 °C was added Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1 mmol) and heated under reflux at 84 °C for two hours and the resulting solution was kept to cool down naturally at room temperature overnight. The complex formed was filtered, washed thoroughly with 5 ml each of water, ethanol and ether and dried *in vacuo* over  $P_4O_{10}$ .

#### 2.3.4. Synthesis of $[Ni(HL^2)_2](ClO_4)_2 \cdot 2H_2O(5)$

To a solution of the HL<sup>2</sup> (1 mmol) 25 ml hot boiling ethanol at 82 °C was added Ni(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (1 mmol) and heated at reflux for one hour and the resulting solution was kept to cool down naturally at room temperature overnight. The complex formed was filtered, washed thoroughly with 5 ml each of water, ethanol and ether and dried *in vacuo* over  $P_4O_{10}$ .

#### 3. Physical measurements

Elemental analyses of the thiosemicarbazones and the complexes were done on a Heracus elemental analyzer at CDRI, Lucknow, India and on a Vario EL III CHNS analyzer at SAIF, Kochi, India. The IR spectra were recorded on a Thermo Nicolet AVATAR 370 DTGS model FT-IR spectrophotometer with KBr pellets at SAIF, Kochi. The far IR spectra were recorded using polyethylene pellets in the 500-100 cm<sup>-1</sup> region on a Nicolet Magna 550 FTIR instrument at the Regional Sophisticated Instrument Facility, Indian Institute of Technology, Bombay, India. Electronic spectra were recorded on a Cary 5000, version 1.09 UV-Vis-NIR spectrophotometer from a solution in CHCl<sub>3</sub> at DAC, CUSAT, Kochi. The magnetic susceptibility measurements were carried out at the Indian Institute of Technology, Roorkee, India, at room temperature in the polycrystalline state on a PAR model 155 Vibrating Sample Magnetometer at 5 kOe field strength. The molar conductivities of the complexes in dimethylformamide solutions (10<sup>-3</sup> M) at room temperature were measured using a direct reading conductivity meter.

# 4. X-Ray crystallography

Single crystals of compounds  $[NiL_2]$ ·DMF (**1a**) and  $[Ni(HL^2)_2](ClO_4)_2$ ·2H<sub>2</sub>O (**5**) of X-ray diffraction quality were

Table 1

Crystal refinement parameters of the complexes 1a, 5& 7a.

$[NiL_{2}^{1}]$ ·DMF ( <b>1a</b> )	$[Ni(HL^2)_2](ClO_4)_2 \cdot 2H_2O(5)$	$[NiL_{2}^{3}] \cdot H_{2}O(7a)$
C <sub>31</sub> H <sub>33</sub> N <sub>9</sub> NiO <sub>3</sub> S <sub>2</sub>	C <sub>30</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>8</sub> NiO <sub>10</sub> S <sub>2</sub>	$C_{24}H_{20}N_{10}Ni_1O_1S_2$
702.49	862.38	587.31
293(2)	100.0(1)	150(2)
0.71073	0.71073	0.71073
Triclinic	Orthorhombic	Monoclinic
ΡĪ	Fddd	I 2/a
10.2850(14)	10.6424(4)	12.7091(6)
10.6120(10)	44.668(3)	9.2346(4)
16.3600(11)	31.2715(15)	21.2265(8)
108.467(6)	90.00	90.00
93.263(8)	90.00	94.311(4)
102.453(9)	90.00	90.00
1638.6(3)	14,865.7(13)	2484.17(18)
2	16	4
1.424	1.541	1.570
0.767	0.844	0.990
732	7136	1208
$0.25\times0.20\times0.15$	$0.78\times0.28\times0.19$	$0.23\times0.18\times0.13$
$-12 \le h \le 0$ ,	$-10 \le h \le 12$ ,	$-15 \le h \le 15$ ,
$-12 \le k \le 12$ ,	$-52 \le k \le 52$ ,	$-10 \le k \le 10$ ,
$-19 \le l \le 19$	$-37 \le l \le 37$	$-25 \le l \le 24$
6106	4259	11,503
5768 [R(int) = 0.0444]	4259 [R(int) = 0.0425]	2187[R(int) = 0.0531]
Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
5768 / 162 / 469	4259/ 5 / 272	2187/1/173
0.998	1.055	1.099
$R_1 = 0.0550, wR_2 = 0.1010$	$R_1 = 0.0238$ , $wR_2 = 0.0448$	$R_1 = 0.0466, wR_2 = 0.1089$
$R_1 = 0.1862, wR_2 = 0.1284$	$R_1 = 0.0239$ , $wR_2 = 0.0449$	$R_1 = 0.0618$ , $wR_2 = 0.1179$
0.304 and -0.395	0.687 and -0.609	0.681 and -0.896
	$\begin{array}{c} [\text{NiL}_2]\text{-DMF} (\textbf{1a}) \\\\\hline\\ C_{31}H_{33}N_9\text{NiO}_3S_2 \\ 702.49 \\ 293(2) \\ 0.71073 \\ \text{Triclinic} \\ P\bar{1} \\\\\hline\\ 10.2850(14) \\ 10.6120(10) \\ 16.3600(11) \\ 108.467(6) \\ 93.263(8) \\ 102.453(9) \\ 1638.6(3) \\ 2 \\ 1.424 \\\\\hline\\ 0.767 \\\hline\\ 732 \\ 0.25 \times 0.20 \times 0.15 \\ -12 \leq h \leq 0, \\ -12 \leq k \leq 12, \\ -19 \leq l < 19 \\ 6106 \\\\\hline\\ 5768 \ [\text{R(int)} = 0.0444] \\ \text{Full-matrix least-squares on } F^2 \\ 5768 \ / 162 \ / 469 \\ 0.998 \\ \text{R}_1 = 0.0550, \ \text{wR}_2 = 0.1010 \\ \text{R}_1 = 0.1862, \ \text{wR}_2 = 0.1284 \\ 0.304 \ \text{and} - 0.395 \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

$$\begin{split} R_1 &= \Sigma ||F_o| - |F_c|| \ / \ \Sigma |F_o| \\ wR_2 &= [\Sigma w(F_o^2 - F_c^2)^2 \ / \ \Sigma w(F_o^2)^2]^{1/2}. \end{split}$$

#### Table 2

Magnetic susceptibilities, molar conductivities and partial elemental analyses of the complexes.

Complex	μ(B.M)	$^{*}\lambda_{M}$	Found (Calc.)%				
			С	Н	Ν	S	
[NiL <sup>1</sup> <sub>2</sub> ]·2H <sub>2</sub> O ( <b>1</b> )	2.88	5	51.13(50.54)	4.46(4.54)	16.50(16.84)	9.58(9.64)	
$[Ni_2L_2^2SO_4] \cdot 1\frac{1}{2}H_2O(2)$	Dia.	19	45.05(44.64)	4.68(4.12)	14.12(13.88)	11.49(11.92)	
$[Ni(HL^2)_2](NO_3)_2 \cdot H_2O \cdot EtOH$ (3)	2.89	160	47.53(47.13)	4.43(4.94)	17.66(17.17)	8.43(7.86)	
$[NiL^{2}(HL^{2})]OAc \cdot 3H_{2}O(4)$	2.86	85	52.35(51.97)	5.07(5.45)	15.46(15.15)	8.19(8.67)	
$[Ni(HL^2)_2](ClO_4)_2 \cdot 2H_2O(5)$	3.09	136	41.71(41.78)	4.07(4.21)	12.94(12.99)	7.56(7.44)	
[NiL <sup>3</sup> OAc]·2 <sup>1</sup> / <sub>2</sub> H <sub>2</sub> O ( <b>6</b> )	Dia.	2	40.34(40.12)	4.52(4.33)	16.48(16.71)	7.74(7.65)	
[N <i>i</i> L <sup>3</sup> NO <sub>3</sub> ]·3H <sub>2</sub> O ( <b>7</b> )	Dia.	20	34.04(33.44)	4.19(3.74)	19.17(19.50)	7.52(7.44)	

\*Molar conductivity of 10<sup>-3</sup> M DMF solution, in ohm<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>.

grown from their DMF and methanol solutions respectively, by slow evaporation at room temperature in air. Single crystals of the complex  $[NiL_2^3] \cdot H_2O$  (7a) were obtained by slow evaporation of a solution of complex 7 in methanol water mixture. The crystallographic data and structure refinement parameters of all the complexes are given in Table 1. The data collection and cell refinement of 1a were carried out using a ARGUS-MACH3 (Nonius, 1997) with graphite monochromated Mo  $K_{\alpha}$  ( $\lambda = 0.71073$  Å) radiation at the National Single Crystal X-Ray Diffraction Facility, IIT, Bombay, India while OXFORD DIFFRACTION XCALIBUR-S was used for 7a. A single crystal of compound 5 is diffracted by a Bruker Smart Apex2 CCD area detector diffractometer equipped with graphite monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation, at the School of Physics, Universiti Sains Malaysia, Penang, Malaysia. The trial structures were solved using SHELXS-97 [16] and refinements were carried out by full-matrix least squares on  $F^2$  (SHELXL-2018/1) [16]. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms on carbon were placed in calculated positions, guided by difference maps and refined isotropically. Nitrogen bound hydrogen atoms were located from Fourier maps and N–H distances were restrained to  $88\pm0.01$  Å. Hydrogens bound to oxygen of water molecule in **7a** could not be located and were ignored in the final stage of refinement. DMF molecule is disordered over two sites with occupancies of 0.578(11) and 0.422(11) for major and minor disordered parts respectively. Perchlorate ions in **5** are disordered over two sites with occupancies of 0.5424(7) and 0.4576(7) for major and minor disordered parts respectively. Molecular graphics employed were ORTEP-III [17], PLATON [18] and Mercury [19].

#### 5. Results and discussion

Compositions and empirical formulae of the seven Ni(II) complexes were determined by using elemental analyses. Molar conductivity measurements, UV-Vis absorption spectra, FT-IR spectra and magnetic susceptibility measurements were also done. The stoichiometries of the complexes with partial elemental analyses, molar conductivity and magnetic susceptibility of the complexes



Fig. 1. ORTEP diagram of the complex 1a in 50% probability ellipsoids. All hydrogen atoms and DMF are omitted for clarity.



Fig. 2. ORTEP diagram of the complex 5 in 50% probability ellipsoids. All hydrogen atoms, water molecules and anions are omitted for clarity.

are presented in Table 2. Molar conductivity measurements show that complexes **1**, **2**, **6**, and **7** are non-electrolytes and the remaining are cationic complexes, behaving either as 1:1 (**4**) or 2:1 (**5**) electrolytes in  $10^{-3}$  M DMF solution. The complexes **2**, **6** and **7** are diamagnetic indicating probable square planar geometry for a normal spin free  $d^8$  system. Complexes **1**, **3**, **4** and **5** are paramagnetic with  $\mu_{eff}/= 2.85 - 3.09$  BM. In the compounds **1**, **2**, **6** and **7**, the thiosemicarbazones deprotonate and chelate in thiolate form. In complexes **3** and **5** the thiosemicarbazones are in the thione form, whereas in **4** both the thione and the deprotonated thiolate forms of the ligand are coordinated, in agreement with IR spectral study.

5.1. Crystal structures of [NiL<sup>1</sup><sub>2</sub>]·DMF (**1a**), [Ni(HL<sup>2</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (**5**) & [NiL<sup>3</sup><sub>2</sub>]·H<sub>2</sub>O (**7a**)

The Ni(II) centers in all the three complexes adopt octahedral geometry by the coordination of the mono deprotonated form of the respective ligands,  $HL^1$  in  $[NiL_2]\cdotDMF$  (**1a**) and  $HL^3$  in  $[NiL_2]\cdotH_2O$  (**7a**), but by the coordination of the neutral ligand  $HL^2$ in  $[Ni(HL^2)_2](CIO_4)_2\cdot2H_2O$  (**5**). The molecular structures of **1a**, **5** and **7a** along with atom numbering schemes are given in Figs. 1-3. The Ni(II) ion in complexes **1a** and **7a** are coordinated in a *meridional* fashion [20,21] using pairs of *cis* pyridyl nitrogen, *trans* azomethine nitrogen and *cis* thiolate sulfur atoms by two monoan-



Fig. 3. ORTEP diagram of the complex 7a in 50% probability ellipsoids. All hydrogen atoms and water molecule are omitted for clarity.

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Selected	bond	lengths	(Å) and	d bond	angles (°)	of HL <sup>2</sup> ,	$[NiL_{2}^{1}]$	DMF	(1a),
[Ni(HL2)-		1)2·2H2O	( <b>5</b> ) and	I [NiL <sup>3</sup> 2	1.H <sub>2</sub> O (7a).				

	*HL <sup>2</sup>	1a	5	7a
S1-C7	1.6849(13)	1.707(5)	1.6982(11)	1.724(3)
S2-C21		1.733(5)		
N2-C6	1.2837(15)	1.289(5)	1.2877(15)	1.287(5)
N6-C20		1.275(6)		
N2- N3	1.3783(14)	1.367(5)	1.3628(13)	1.378(4)
N6-N7		1.367(5)		
N3-C7	1.3587(16)	1.332(6)	1.3578(15)	1.321(4)
N7-C21		1.322(6)		
N4-C7	1.3401(16)	1.375(6)	1.3320(15)	1.375(5)
N8-C21		1.360(6)		
Ni1-S1		2.3899(15)	2.4416(3)	2.3996(10)
Ni1-S2		2.4028(15)		
Ni1-N1		2.101(4)	2.0927(10)	2.117(3)
Ni1-N5		2.107(4)		
Ni1-N2		2.028(4)	2.0357(9)	2.020(3)
Ni1-N6		2.021(5)		
C6-N2-N3	114.37(10)	118.6(4)	120.93(10)	117.9(3)
N2-N3-C7	120.47(10)	110.8(4)	119.41(9)	112.0(3)
N4-C7-N3	116.16(10)	117.1(5)	115.12(10)	118.0(3)
N3-C7-S1	119.25(8)	127.7(4)	121.75(9)	126.6(3)
N4-C7-S1	124.59(9)	115.1(4)	123.2(7)	115.4(3)
N1-Ni1-N5		90.08(15)		
N1-Ni1-N1a			93.66(5)	86.61(16)
N2-Ni1-N6		173.06(16)		
N2-Ni1-N2a			174.93(5)	179.02(16)
S1-Ni1-S2		96.37(6)		
S1-Ni1-S1a			95.615(15)	96.19(5)
S1-Ni1-N1		159.08(12)	158.78(3)	158.51(8)
S1-Ni1-N5		92.02(11)		
S1-Ni1-N2		80.41(12)	81.29(3)	80.47(8)
S1–Ni1–N2a			102.17(3)	100.20(8)
S1-Ni1-N6		105.10(11)		
N1-Ni1-N2		78.68(16)	77.48(4)	78.64(11)
N1-Ni1-N2a			98.99(4)	100.63(11)
N1-Ni1-N6		95.71(16)		
N1-Ni1-S2		88.95(11)		
N1-Ni1-S1a			89.25(3)	92.39(8)
N2-Ni1-N5		97.18(16)		
N2-Ni1-S2		103.31(12)		
S2-Ni1-N5		158.87(12)		
S2-Ni1-N6		80.49(13)		
N5-Ni1-N6		78.60(17)		
*Ref [15].				

ionic ligands. In complex 5, two molecules of the neutral ligand HL<sup>2</sup> are coordinated in the *meridional* fashion [20] using pairs of *cis* pyridyl nitrogen, trans azomethine nitrogen and cis thione sulfur atoms. Heterocyclic thiosemicarbazones show a strong tendency for this meridional coordination and is seen in most of their octahedral metal complexes, resulting in two bicyclic chelate systems. In complex 1a, the bicyclic chelate systems Ni1, S1, C7, N3, N2, C6, C5, N1 and Ni1, S2, C21, N7, N6, C20, C19, N5 are approximately planar as evidenced by the maximum deviation of 0.0618(16) Å for S1 and 0.055(4) Å for N5 respectively. Half of the complex molecules of 5 and 7a were generated by symmetry. The bicyclic chelate system Ni1, S1, C7, N3, N2, C6, C5, N1 in complex 5 is approximately planar with a maximum deviation of -0.0546(9) Å for N1, while the same system in complex 7a is also planar with maximum deviation of 0.087(3) Å for N1. The dihedral angle formed by the mean planes of the bicyclic chelate systems of each of the ligands is  $86.28(12)^{\circ}$  in **1**,  $84.56(3)^{\circ}$  in **5** and  $87.64(8)^{\circ}$  in **7a**. The bond lengths Ni– $N_{azomethine},$  Ni– $N_{py},$  and Ni–S in all the complexes increases in that order as in similar compounds [19-22]. In compound 1, the trans angles N1-Ni1-S1, N5-Ni1-S2 and N2-Ni1-N6 are 159.08(12), 158.87(12) and 173.06(16)° respectively, while these angles N1-Ni1-S1 and N2-Ni1-N2a are 158.77(3) and 174.93(5)° in complex 5 and 158.51(8) and 179.02(16)° in complex 7a respectively. These factors suggest considerable distortion from an octahedral geometry around Ni(II) center in all the complexes, but lesser in complex 7a.

In compound 5, the ligand HL<sup>2</sup> undergoes structural reorientation to coordinate to the metal in an NNS manner. The azomethine nitrogen, was in *E* configuration with both pyridyl nitrogen and thione sulfur atoms in its metal free form of ligand [15], is now in Z form with pyridine nitrogen and sulfur atoms. The C-S bond length increases slightly by 0.0133(13) Å and the N3-C7 bond length remains almost same on coordination, in agreement with the coordination *via* thione form of the ligand. In complex **1a**, the C-S {1.707(5) Å for C7-S1 and 1.733(5) Å for C21-S2} and C-N {1.332(6) Å for N3–C7 and 1.322(6) Å for C21–N7} bond lengths are consistent with partial single and double bond character confirming the coordination via thiolate sulfur after deprotonation. Similar bonding in complex 7a is also evidenced by the C-S {1.724(3) Å for C7–S1} and C–N {1.321(4) Å for N3–C7} bond lengths. The Ni-Nazomethine bond lengths are less compared to Ni-Npvridine, indicating the higher strength of former bond than the latter in all



Fig. 4. A view of the packing of molecules of 1a along the *c* axis showing hydrogen bonding interactions.



Fig. 5. A view of the unit cell packing of the molecule 5 along the *a* axis showing ABABAB... packing along the c axis.

Interaction parameters of [NiL12]·DMF (1a).

$\pi$ - $\pi$ interactions			
Cg(I)…Cg(J)	Cg…Cg (Å)	α (°)	β (°)
$Cg(5) Cg(7)^a$	3.671(3)	3.8(3)	24.3
$Cg(6) Cg(8)^{b}$	3.711(3)	3.3(3)	27.6
$Cg(7) \cdot Cg(5)^{c}$	3.670(3)	3.8(3)	21.7
$Cg(8) \cdot Cg(6)^{b}$	3.711(3)	3.3(3)	24.5
C–H $\cdots\pi$ interactions			

C23-H23· Cg(1) <sup>e</sup>	3.00	3.814(6)	147
C15–H15· Cg(1) <sup>d</sup>	2.99	3.323(6)	103
$C1-H1\cdots Cg(2)^d$	2.92	3.244(7)	102
C–H…Cg(J)	H–Cg (Å)	C-Cg (Å)	C-H…Cg (°)

Cg(1)= Ni1, S1, C7, N3, N2; Cg(2)= Ni1, S2, C21, N7, N6; Cg(5)= N1, C1, C2, C3, C4, C5; Cg(6)= N5, C15, C16, C17, C18, C19; Cg(7)= C8, C9, C10, C11, C12, C13; Cg(8)= C22, C23, C24, C25, C26, C27,  $\alpha$  (°)=Dihedral angle between planes I and J@ $\beta$  (°)=Angle between Cg(I)-Cg(J) vector and Cg(J) perp

Hydrogen bonding interactions								
D-H ·A	D-Н (Å)	H–A (Å)	D-A (Å)	D-H ·A (°)				
N4-H4'····O3 <sup>f</sup>	0.88(3)	2.07(4)	2.889(16)	155(4)				
N4–H4'····O3A <sup>f</sup>	0.88(3)	2.20(4)	3.042(19)	162(4)				
N8-H8···S2 <sup>e</sup>	0.88(3)	2.58(4)	3.371(6)	151(4)				
C3-H3O2 <sup>g</sup>	0.93	2.55	3.416(8)	156				
C4-H4-01 <sup>h</sup>	0.93	2.60	3.269(7)	129				
C9-H9N3	0.93	2.29	2.893(7)	122				
C13-H13-03 <sup>f</sup>	0.93	2.40	3.185(14)	142				
C20-H20S1 <sup>b</sup>	0.93	2.82	3.692(5)	156				
C27-H27N7	0.93	2.26	2.866(6)	122				
D = donor, A = acceptor, Equivalent position codes a = -x, 1+y, z; b = -x, -y, -z; c = x, -1+y, z; d = x. y, z; e = 1-x, -y, -z; f = -1+x, -1+y, z; g = 1-x, 1-y, -z, h = 1-x, -y, -z; f = -1+x, -1+y, z; f = -1+x, -1+								

#### Table 5

Interaction pa	rameters of	[Ni(HL <sup>2</sup> ]	)2](	$(ClO_4)$	$)_2 \cdot 2H_2O$	(5	)
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C–H $\cdots$ $\pi$ interactions								
C−H…Cg(J)	H…Cg (Å)	C–Cg (Á)		C-H…Cg (°)				
C1-H1…Cg(1) <sup>a</sup>	2.95	3.2744(13)		102				
C1-H1…Cg(3) <sup>b</sup>	2.95	3.2744(13)		102				
Cg(1)=Ni1, S1, C7, N3, N2; Cg	(3)= Ni1, S1a, C7a, N3a, N	2a.						
Hydrogen bonding interactions	;							
D-H…A	D-H (Å)	H…A (Å)	D-A (Å)	D−H…A (°)				
O1S-H1A…N3 <sup>b</sup>	0.837(13)	2.204(14)	2.7827(13)	126.4(12)				
O1S-H1B…O3A <sup>b</sup>	0.845(14)	2.086(14)	2.830(2)	146.6(14)				
N3-H3'…O1S <sup>b</sup>	0.872(9)	1.950(10)	2.7827(13)	159.3(14)				
N4–H4'…O3B <sup>b</sup>	0.932(9)	2.292(10)	3.171(2)	157.1(13)				
N4-H4'…O4A <sup>b</sup>	0.932(9)	2.171(13)	2.903(6)	134.8(13)				
C2-H2O2B <sup>c</sup>	0.93	2.46	3.371(3)	165				
C3-H3···O2B <sup>d</sup>	0.93	2.52	3.239(3)	134				
C8-H8AS1	0.97	2.76	3.1091(15)	102				
D = donor, A = acceptor, Equiva	D = donor, A = acceptor, Equivalent position codes a = 3/4-x, -1/4-y, z; b = x, y, z; c = 1-x, -1/4+z, - 1/4+-z; d = 3/4+x,-y, -1/4+z.							

the complexes. The Ni–S bond length in complex **5** is higher compared to that in **1** and **7a**, is in agreement with thione coordination (Table 3).

In complex **1a**, the molecules are connected by various hydrogen bonding interactions (Fig. 4) and are packed in the lattice in a 'face to face' arrangement along the *a* axis. The crystal structure cohesion is reinforced by making use of  $\pi$ - $\pi$  and C-H… $\pi$  ring interactions. Relevant hydrogen bonding, C-H… $\pi$  and  $\pi$ - $\pi$  ring interactions of the complex **1a** are given in Table 4.

The molecules of **5** are packed in a 'face to face' ABABAB... manner along the *c* axis within the unit cell (Fig. 5), as a result of diverse hydrogen bonding and C-H... $\pi$  ring interactions (Table 5). The 'face to face' ABABAB...manner packing is seen in the crystal lattice of complex **7a** also, but is along the *b* axis (Fig. 6). Various hydrogen bonding and  $\pi \cdots \pi$  ring interactions of complex **7a** are given in Table 6. In the crystal packing of complex **5**, no significant  $\pi$ - $\pi$  interactions are observed, while the lattice cohesion of complex **7a** lacks relevant C-H... $\pi$  interactions.

# 5.2. Infrared spectra

The IR spectral bands are found helpful to decide the coordination modes, which are listed in Tables 7 and 8. In the IR spectra of complexes **3** and **5**, bands at 3204 and 3234  $\text{cm}^{-1}$  regions are due to the stretching frequency for <sup>2</sup>NH. Besides, no band due to the SH group is observed between 2600 and 2500  $\mbox{cm}^{-1}$  in agreement with the thione form of the ligand in these complexes [23]. In the spectra of the complexes **1**, **2**, **6** and **7**,  $\nu$ (<sup>4</sup>NH) vibrations appear in the range 3312-3440 cm<sup>-1</sup>, but there is no band corresponding to stretching of the hydrazine NH, consistent with deprotonation of the ligands in these complexes. The shift of the thiocarbonyl stretching and bending modes to lower frequencies in all the complexes is in accordance with the coordination through sulfur. The  $\nu$ (Ni–S) bands in the 325 – 375 cm<sup>-1</sup> regions further confirm the sulfur coordination [23]. A similar shift of  $\nu$ (C=N) frequencies corroborate coordination of the azomethine nitrogen [20]. Additional evidence for coordination of the imine nitrogen is the presence of

Interaction parameters of [NiL<sup>3</sup><sub>2</sub>]·H<sub>2</sub>O (7a).

$\pi$ —- $\pi$ interactions								
Cg(I)…Cg(J)	Cg-Cg(Å)	α°		$eta$ $^\circ$				
$Cg(5)\cdots Cg(6)^{a}$	3.903(2)	18.43(18)		20.1				
$Cg(6)\cdots Cg(5)^{b}$	3.903(2)	18.43(18)		37.7				
Cg(5)= N1, C1, C2, C3, between Cg(I)-Cg(J) ve	$Cg(5)=$ N1, C1, C2, C3, C4, C5; $Cg(6)=$ N5, C8, C9, C10, C11, C12, $\alpha$ (°)=Dihedral angle between planes I and J, $\beta$ (°)=Angle between $Cg(I)-Cg(J)$ vector and $Cg(J)$ perp							
Hydrogen bonding inte	ractions							
D-H…A	D-Н (Å)	H…A (Å)	D-A (Å)	D-H…A (°)				
N4–H4N…N5 <sup>c</sup>	0.87(4)	2.43(4)	3.299(4)	175(3)				
C4-H40111	0.95	2.49	3.429(4)	171				
C6-H6…S1 <sup>d</sup>	0.95	2.73	3.628(4)	157				
C9-H9N3	0.95	2.25	2.852(4)	120				
C9-H9S1 <sup>b</sup>	0.95	2.84	3.623(4)	140				
C12-H12S1c	0.95	2.77	3.602(4)	146				

 $D = donor, A = acceptor, Equivalent position codes a = -1/2 + x, -y, z; b = \frac{1}{2} + x, -y, z; c = \frac{3}{2} - x, -\frac{1}{2} - y, -\frac{1}{2} - z; d = 1 - x, -y, -z.$ 



Fig. 6. A view of the unit cell packing of the molecule 7a along the *a* axis showing different hydrogen bonding interactions.

 $\nu$ (Ni–N) bands in the 417-/430 cm<sup>-1</sup> range [23,24]. A second band due to  $\nu$ (C=N) is resolved in the spectra of **1**, **2**, **4**, **6** and **7** at *ca*. 1600 cm<sup>-1</sup>. Coordination of the pyridine nitrogen atom is clearly shown by the shift to higher frequencies of the deformation mode bands that appear in the ranges 613–622 and 401 - 412 cm<sup>-1</sup> in the spectra of HL<sup>1</sup>, HL<sup>2</sup> and HL<sup>3</sup> [25]. The  $\nu$ (M–N) bands for the pyridyl nitrogen are assigned in the 211–272 cm<sup>-1</sup> region, confirm the coordination of pyridine nitrogen. The sulfato complex **2** exhibits a medium band at 977 cm<sup>-1</sup> due to  $v_1$ , a medium band at 451 cm<sup>-1</sup> due to  $v_2$ , medium and weak bands at 1185, 1118 and 1023 cm<sup>-1</sup> corresponding to  $v_3$ , and weak band at 609 cm<sup>-1</sup> due to  $v_4$ , which are assigned to the coordination of bidentate sulfate group [26].

In the spectrum of the complex **3**, the absence of the combination bands ( $\nu_1$  +  $\nu_4$ ) in the region 1700–1800 cm<sup>-1</sup> rules out

Table 7

Infrared spectral data	(cm <sup>-1</sup>	<sup>1</sup> ) of the	ligands	and	their	complexes
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Compound	$\nu(C = N)$	$\nu(N = C)$	ν(N-N)	$\nu/\delta(C-S)$	py(ip)	py(op)	$\nu(^{2}N-H)$	$\nu(^{4}N-H)$
HL <sup>1</sup>	1584		1024	1334,837	613	401	3134	3310
$[NiL_{2}^{1}] \cdot 2H_{2}O(1)$	1566	1608	1133	1300,829	646	409	_	3440
HL <sup>2</sup>	1586		1079	1324,897	622	406	3129	3374
$[Ni_2L_2^2SO_4] \cdot 1\frac{1}{2}H_2O(2)$	1534	1624	1143	1338.894	670	438	_	3312
$[Ni(HL^2)_2](NO_3)_2 \cdot H_2O \cdot EtOH (3)$	1575	_	1156	1302,886	637	425	3234	3428
$[NiL^{2}(HL^{2})]OAc \cdot 3H_{2}O(4)$	1576	1600	1135	1310,891	637	417	_	3419
$[Ni(HL^2)_2](ClO_4)_2 \cdot 2H_2O(5)$	1570	_	1143	1310,886	637	425	3204	3424
HL <sup>3</sup>	1593		1078	1298,929	614	412	3057	3310
$[NiL^{3}OAc] \cdot 2\frac{1}{2}H_{2}O(6)$	1537	1612	1126	1277,903	641	421	_	3411
$[NiL^3NO_3]$ ·3H <sub>2</sub> O ( <b>7</b> )	1568	1608	1159	1260,897	640	416	_	3416

Metal-ligand stretching frequencies (cm<sup>-1</sup>) of the complexes.

Complexes	vNi-N <sub>azo.</sub>	vNi-N <sub>py</sub>	vNi-S
$[NiL_{2}^{1}]\cdot 2H_{2}O(1)$	417	245	372
$[Ni_2L_2^2SO_4] \cdot 1\frac{1}{2}H_2O(2)$	425	228	358
$[Ni(HL^2)_2](NO_3)_2 \cdot H_2O \cdot EtOH (3)$	430	248	375
$[NiL^{2}(HL^{2})]OAc \cdot 3H_{2}O(4)$	412	271	325
$[Ni(HL^2)_2](ClO_4)_2 \cdot 2H_2O(5)$	427	211	371
[NiL <sup>3</sup> OAc]·2½H <sub>2</sub> O ( <b>6</b> )	428	220	345
$[NiL^3NO_3] \cdot 3H_2O(7)$	427	225	355

the possibility for coordinated nitrato group. The bands at *ca*. 830 cm<sup>-1</sup> ( $\nu_2$ ), 1380 cm<sup>-1</sup> ( $\nu_3$ ) and 700 cm<sup>-1</sup> ( $\nu_4$ ) clearly point out the uncoordinated nature of the nitrato group [12].

The nitrato complex **7** has two strong bands at 1260 and 1383 cm<sup>-1</sup> with a separation of 123 cm<sup>-1</sup> corresponding to  $v_1$  and  $v_4$  indicating the presence of a terminal monodentate nitrato group [27]. The  $v_1+v_4$  combination bands, considered as diagnostic for

the monocoordinated nitrato group, are observed at 1713 and 1738  $\rm cm^{-1}.$ 

The spectrum of the acetate-containing complex **4** displays relatively strong bands at 1559 due to  $\nu_a(COO)$  and 1417 cm<sup>-1</sup> due to  $\nu_s(COO)$  indicating the ionic nature of the acetate in this compound [28]. In complex **6** strong bands observed at 1570 and 1400 cm<sup>-1</sup> are assigned to  $\nu_a(COO)$  and  $\nu_s(COO)$ , which support the unidentate nature of acetate group [28].

The perchlorate complex **5** shows single broad band at 1122 cm<sup>-1</sup> and strong bands at 637 and 624 cm<sup>-1</sup>, indicating the presence of ionic perchlorate. The bands at 1122 cm<sup>-1</sup> are assignable to  $\nu_3$ (ClO<sub>4</sub>) and, a medium band at 915 cm<sup>-1</sup> may be assigned to  $\nu_1$ (ClO<sub>4</sub>) of the perchlorate ion [11].

# 5.3. Electronic spectra

The high-energy  $\pi \rightarrow \pi^*$  transitions *ca.* 42,000 cm<sup>-1</sup> are not significantly altered on complex formation. The  $n \rightarrow \pi^*$  transitions as-



Fig. 7.  $d_{norm}$  surface view, shape index and curvedness of complex a) [NiL1<sub>2</sub>]·DMF (1a), b) [Ni(HL<sup>2</sup>)<sub>2</sub>] (ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (5) and c) [NiL3<sub>2</sub>] ·H<sub>2</sub>O(7a).



Fig. 8. 2D finger print plots of complex a) [NiL<sup>1</sup><sub>2</sub>] (1), b) [Ni(HL<sup>2</sup>)<sub>2</sub>] (5) and c) [NiL<sup>3</sup><sub>2</sub>] (7a) showing the percentage of contacts contributed to the total Hirshfeld surface area.

 Table 9

 Electronic spectral data (cm<sup>-1</sup>) of the ligands and their complexes.

Compound	$\pi \! \rightarrow \! \pi^*$	$n \rightarrow \pi^*$	СТ	d-d
HL <sup>1</sup>	42,730,38,760	30,770	_	_
$[NiL_{2}^{1}]\cdot 2H_{2}O(1)$	41,800,37,880	32,360	22,620	11,590
HL <sup>2</sup>	42,190,36,630	30,960	_	-
$[Ni_2L_2^2SO_4] \cdot 1\frac{1}{2}H_2O(2)$	42,200,38,310	33,010	22,320	17,010
$[Ni(HL^2)_2](NO_3)_2 \cdot H_2O \cdot EtOH (3)$	42,120,38,610	32,220	22,570	11,860
$[NiL^{2}(HL^{2})]OAc \cdot 3H_{2}O(4)$	41,600,37,910	33,110	22,108	18,910
$[Ni(HL^2)_2](ClO_4)_2 \cdot 2H_2O(5)$	42,300,37,740	33,070	22,420	18,180
HL <sup>3</sup>	41,840,35,840	29,500	_	-
$[NiL^{3}OAc] \cdot 2\frac{1}{2}H_{2}O(6)$	42,200,35,910	32,100	22,230	_
$[NiL^3NO_3] \cdot 3H_2O(7)$	41,900,38,020	32,210	22,070	-

sociated with the azomethine functions of the thiosemicarbazone moieties are shifted to higher energy for the complexes [29].

The ground state of Ni(II) in an octahedral coordination is  ${}^{3}A_{2g}$ . Electronic spectral bands of hexacoordinate compounds of nickel(II) can be assigned to the three spin allowed transitions  ${}^{3}T_{2g}(F) \leftarrow {}^{3}A_{2g}(F) (\nu_1)$ ,  ${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}(F) (\nu_2)$  and  ${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F) (\nu_3)$  in the increasing order of energy with molar absorptivity generally below 20. The  $\nu_3$  band is often masked by the high-intensity charge transfer bands [20]. The energy of the  $\nu_1$  is equal to 10 Dq. It is found that the spectra of the octahedral complexes **1**, **3**, **4** and **5** do not resolve to get all the three bands possible. Table 9 shows the band maxima of electronic transitions for the ligands and their complexes in chloroform solutions. The bands at *ca*.12000 cm<sup>-1</sup> are assigned to  $\nu_2$ . But  $\nu_3$  is presumably obscured by the weak charge transfer bands at *ca*.23000 cm<sup>-1</sup> [29].

Diamagnetism in Ni(II) complexes is a consequence of eight electrons being paired in the four low-lying *d* orbitals, the upper orbital being  $d_x^2$ - $y^2$ . The four lower orbitals are often so close in energy that individual transitions from them to the upper *d* level cannot be distinguished resulting in a single absorption band. The very weak band at *ca.* 19,000 cm<sup>-1</sup> corresponds to the *d*-*d* bands of the complexes **2**, **6** and **7**. A weak shoulder at *ca.*23000 cm<sup>-1</sup> is assigned to charge transfer transition.

# 5.4. Hirshfeld surface analysis of $[NiL_2]$ ·DMF (**1a**), $[Ni(HL_2)_2](ClO_4)_2$ ·2H<sub>2</sub>O (**5**) & $[NiL_2]$ ·H<sub>2</sub>O (**7a**)

The Hirshfeld surface analyses of the complexes **1a**, **5** and **7a** were performed using the program Crystal Explorer 17.5 [30]. The Hirshfeld  $d_{norm}$ , shape index and curvedness surfaces of all complexes were mapped (Fig. 7). The two-dimensional decomposed fingerprint plots were also plotted (Fig. 8) to understand and confirm the supramolecular interactions quantitatively [31,32].

The hydrogen bonding interactions are evidenced by intense red coloured spots on the Hirshfeld surface mapped with  $d_{norm}$  functions. A number of small red spots is also visible indicating short H…H contacts, which is clearer on  $d_{norm}$  surfaces of the complexes **1** and **7a**. Presence of blue triangles (bow-tie pattern) in the shape index surface and the flat surfaces on the aromatic rings in the curvedness indicate the presence of  $\pi$ - $\pi$  stacking interactions in the lattice, which are more and clear in the complexes **1a** and **7a**. The red regions of the Hirshfeld surface mapped over shape index properties of complexes **1** and **5** are indicating the C–H… $\pi$  interactions in their crystal lattices. These measures of curvature provide clear insight on molecular packing in the crystal.

Attributes of Hirshfeld surfaces of the Ni(II) thiosemicarbazone complexes.

Complex	Volume (Å <sup>3</sup> )	Area (Å <sup>2</sup> )	Globularity (G)	Asphericity $(\Omega)$
$ \begin{array}{l} [\text{NiL}_2] \cdot \text{DMF} \ (\textbf{1a}) \\ [\text{Ni}(\text{HL}^2)_2](\text{CIO}_4)_2 \cdot 2\text{H}_2\text{O} \ (\textbf{5}) \\ [\text{NiL}_2_2] \cdot \text{H}_2\text{O} \ (\textbf{7a}) \end{array} $	690.67	592.45	0.638	0.275
	708.01	608.69	0.631	0.090
	590.82	517.28	0.658	0.124

The 2D fingerprint plots clearly analyze and display the various intermolecular interactions in the crystal lattices. The H...H interactions (van der Waals forces) are observed as the most dominant forces in all the complexes and are found in the middle of the scattered point of the 2D fingerprint plots. The percentage of H...H contacts contributed to the total Hirshfeld surface area is 46.1, 37.2 and 37.4% for the complexes 1a, 5 and 7a respectively. The relative contribution of other significant interactions observed for the complex 1a are C.-.H (21.4%), S.-.H (9.9%), O.-.H (9.3%), N.-.H (6.8%) and C...C (4.7%); while that of complex 5 are O...H (23.3%), C...H (22.1%), S.-.H (6.7%), N.-.H (4.2%) and C.-.C (3.5%). These relative contributions for the complex **7a** are C.-.H (20.2%), N.-.H (17.2%), S...H (9.0%), C...C (6.4%) and O...H (4.0%). The C-C interaction is a measure of the  $\pi \cdots \pi$  stacking interaction and is found most in complex 7a, followed by complex 1a. The C-H interactions, may be considered as a measure of C–H… $\pi$  interactions, are also found strong in all the complexes and reinforces the crystal structure cohesion.

Comparison of the Hirshfeld volume and surface area of the coordination spheres of the three complexes (Table-10) shows a more crowded environment for the complex **7a** compared with others, as evidenced by their lower value and is mainly because of the absence of perchlorate ion or DMF in the lattice. Globularity is a measure of the degree of deviation of the surface area from that of a sphere of an analogous volume. The lower globularity and the asphericity values indicating deviation from spherical surface and symmetry and more structured molecular surfaces for all the three complexes.

# Supplementary information

Crystallographic data for the structural analysis of the compounds **1a**, **5** and **7a** have been deposited with the Cambridge Crystallographic Data Center, CCDC 276629, CCDC 622321 and CCDC 2044373, respectively. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or e-mail: deposit@ccdc.cam.ac.uk.

# **Declaration of Competing Interest**

The authors declare that "there are no conflicts of interest to declare".

### **CRediT** authorship contribution statement

**P.F. Rapheal:** Conceptualization, Methodology, Writing - original draft. **E. Manoj:** Data curation, Writing - review & editing, Visualization, Investigation. **M.R. Prathapachandra Kurup:** Supervision, Writing - review & editing. **Hoong-Kun Fun:** Investigation, Validation.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.130362.

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