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STRUCTURAL STUDIES OF NICKEL(II) COMPLEXES WITH 1-*TERT*-BUTYLIMIDAZOLE-2-THIONE AND 3-PHENYL-5-METHYL-PYRAZOLE LIGANDS

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The nickel(II) complexes dichlorobis(1-*tert*-butylimidazole-2-thione)nickel(II)  $[\text{Ni}(\text{tm}^{\text{t-Bu}})_2\text{Cl}_2]$  (**1**), dinitratobis(1-*tert*-butylimidazole-2-thione)nickel(II)  $[\text{Ni}(\text{tm}^{\text{t-Bu}})_2(\text{NO}_3)_2]$  (**2**), dichlorobis(3-phenyl-5-methyl-pyrazole)(1-*tert*-butylimidazole-2-thione)nickel(II)  $[\text{Ni}(\text{pz}^{\text{Ph,Me}}\text{H})_2 \times (\text{tm}^{\text{t-Bu}})_2\text{Cl}_2]$  (**3**) and dinitratobis(3-phenyl-5-methyl-pyrazole)(1-*tert*-butylimidazole-2-thione)nickel(II)  $[\text{Ni}(\text{pz}^{\text{Ph,Me}}\text{H})_2(\text{tm}^{\text{t-Bu}})_2(\text{NO}_3)_2]$  (**4**) have been synthesized and studied. The single crystal X-ray diffraction analysis was carried out for **1** and **4** {Bruker Kappa Apex-II CCD diffractometer,  $\text{MoK}_\alpha$  radiation}. Crystal data for **1**: monoclinic  $C2/c$ ,  $a = 16.949(2) \text{ \AA}$ ,  $b = 8.6647(10) \text{ \AA}$ ,  $c = 15.461(3) \text{ \AA}$ ,  $\beta = 117.662(4)^\circ$ ,  $V = 2011.1(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.460 \text{ g/cm}^3$ . Crystal data for **4**: triclinic  $P-1$ ,  $a = 9.9775(7) \text{ \AA}$ ,  $b = 11.2254(8) \text{ \AA}$ ,  $c = 14.8068(10) \text{ \AA}$ ,  $\alpha = 75.401(4)^\circ$ ,  $\beta = 87.422(4)^\circ$ ,  $\gamma = 74.874(4)^\circ$ ,  $V = 1548.86(19) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.405 \text{ g/cm}^3$ . Coordination core of complex **1** adopts distorted tetrahedral geometry whereas core **4** has distorted octahedral geometry. The bonded nitrates are of two types coordinating as monodentate and bidentate ligands.

**Keywords:** synthesis, 1-*tert*-butylimidazole-2-thione, nickel(II), 3-phenyl-5-methyl-pyrazole, non-covalent interactions.

## INTRODUCTION

2-Thioimidazole (N,N,S donor) and its alkyl derivatives have antithyroid activity and platelet inhibitory effects. These compounds also have immuno-modulating and/or cytokine-release-inhibiting action and are therefore suitable for treating disorders associated with a disturbed immune system [ 1, 2]. In recent year, metal complexes have been reported as building blocks in the assembly of poly(thioimidazolyl)borates [ 3—7 ]. The structurally characterized transition metal complexes of thioimidazole are very rare in the literature [ 8—11 ]. In the reported complexes the ligands are coordinated through both sulphur and nitrogen atoms.

The aim of this work was to see how the presence of both 1-*tert*-butylimidazole-2-thione and 3-phenyl-5-methyl-pyrazole would affect the structural properties of the resulting nickel complexes. The present paper reports the structurally characterized nickel complexes with 1-*tert*-butylimidazole-2-thione and 3-phenyl-5-methyl-pyrazole as these types of complexes are not available in the literature except for some complexes with  $\text{N}_2\text{S}$  donor (borate salt) [ 12—16 ].

## EXPERIMENTAL

All solvents used were purified by the literature methods [ 17 ]. The reagents of the highest grade commercially available were used without further purification. All manipulations were carried out in air. 3-Phenyl-5-methyl-pyrazole  $[\text{pz}^{\text{Ph,Me}}\text{H}$ ;  $\text{C}_{10}\text{H}_{10}\text{N}_2$ ] [ 18 ] and 1-*tert*-butylimidazole-2-thione  $[\text{tm}^{\text{t-Bu}}$ ;  $\text{C}_7\text{H}_{12}\text{N}_2\text{S}$ ] [ 19 ] were synthesized according to the literature methods.

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Table 1

Crystal Data, Details of Experiment and Refinement for Complexes **1** and **4**

Compound	Ni(tm <sup>t-Bu</sup> ) <sub>2</sub> Cl <sub>2</sub> <b>1</b>	Ni(pz <sup>Ph,Me</sup> H) <sub>2</sub> (tm <sup>t-Bu</sup> )(NO <sub>3</sub> ) <sub>2</sub> <b>4</b>
Empirical formula	C <sub>14</sub> H <sub>24</sub> N <sub>4</sub> S <sub>2</sub> Cl <sub>2</sub> Ni	C <sub>27</sub> H <sub>32</sub> N <sub>8</sub> O <sub>6</sub> SNi
Formula weight	442.10	655.37
Temperature, K	100	100
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
Unit cell dimension		
<i>a</i> , <i>b</i> , <i>c</i> , Å	16.949(2), 8.6647(10), 15.461(3)	9.9775(7), 11.2254(8), 14.8068(10)
α, β, γ, deg.	90, 117.662(4), 90	75.401(4), 87.422(4), 74.874(4)
<i>V</i> , Å <sup>3</sup>	2011.1(5)	1548.86(19)
<i>Z</i>	4	2
Calculated density, g/cm <sup>3</sup>	1.460	1.405
Absorption coefficient, mm <sup>-1</sup>	1.441	0.746
Crystal dimensions, mm	0.25×0.21×0.19	0.22×0.19×0.11
θ range for data, deg.	2.71—37.31	1.94—33.24
Reflections collected	23809	30449
Data / restraints / parameters	5212 / 0 / 112	11894 / 0 / 393
GOOF on <i>F</i> <sup>2</sup>	1.937	0.857
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0293, <i>wR</i> <sub>2</sub> = 0.0523	<i>R</i> <sub>1</sub> = 0.0416, <i>wR</i> <sub>2</sub> = 0.1125
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0498, <i>wR</i> <sub>2</sub> = 0.0539	<i>R</i> <sub>1</sub> = 0.0769, <i>wR</i> <sub>2</sub> = 0.1476
CCDC deposition number	690450	690451

**Synthesis of Ni(tm<sup>t-Bu</sup>)<sub>2</sub>Cl<sub>2</sub> (1):** NiCl<sub>2</sub>·6H<sub>2</sub>O (0.12 g, 0.5 mmol) and 1-*tert*-butylimidazole-2-thione (0.16 g, 1.0 mmol) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) and CH<sub>3</sub>OH (3 ml) for 1 h. The reaction mixture was filtered through celite and the solvent from the solution was removed to dryness under vacuum. The powdered compound in 76 % yield (0.17 g, 0.38 mmol) was dissolved in CH<sub>3</sub>CN (5 ml) and green crystals were obtained at -20 °C after seven days. Anal. Calc. (%) for C<sub>14</sub>H<sub>24</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub>Ni: C 38.00, H 5.43, N 12.67. Found (%): C 38.02, H 5.48, N 12.61. IR (KBr, cm<sup>-1</sup>): ν(C=S) 1625. UV-Vis (CH<sub>3</sub>CN, λ<sub>max</sub>, nm, ε/M<sup>-1</sup>cm<sup>-1</sup>): 282 (867), 517 (253). μ<sub>eff</sub> = 3.91 B.M. at 295 K.

**Synthesis of Ni(tm<sup>t-Bu</sup>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (2):** To a solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.14 g, 0.5 mmol) in CH<sub>3</sub>OH (5 ml), another solution, of 1-*tert*-butylimidazole-2-thione in CH<sub>2</sub>Cl<sub>2</sub> (10 ml), was added and the mixture was stirred for 1 h. The green solution was filtered through celite and the solvent was evaporated to dryness under vacuum. The crystalline compound in 68 % yield (0.16 g, 0.34 mmol) was obtained. Anal. Calc. (%) for C<sub>14</sub>H<sub>24</sub>N<sub>6</sub>S<sub>2</sub>O<sub>6</sub>Ni: C 34.00, H 4.86, N 17.00. Found (%): C 34.12, H 4.95, N 17.09. IR (KBr, cm<sup>-1</sup>): ν(C=S) 1622, ν<sub>as</sub>(NO<sub>3</sub>) 1528, ν<sub>s</sub>(NO<sub>3</sub>) 1264. UV-Vis (CH<sub>3</sub>CN, λ<sub>max</sub>, nm, ε/M<sup>-1</sup>cm<sup>-1</sup>): 280 (912), 511 (218). μ<sub>eff</sub> = 3.20 B.M. at 295 K.

**Synthesis of Ni(pz<sup>Ph,Me</sup>H)<sub>2</sub>(tm<sup>t-Bu</sup>)Cl<sub>2</sub> (3):** NiCl<sub>2</sub>·6H<sub>2</sub>O (0.12 g, 0.5 mmol), 1-*tert*-butylimidazole-2-thione (0.08 g, 0.5 mmol) and 3-phenyl-5-methyl-pyrazole (0.16 g, 1.0 mmol) were dissolved in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (15 ml) and CH<sub>3</sub>OH (5 ml) and the mixture was stirred for 2 h. The resulting green solution was filtered through celite and solvent was evaporated to dryness under vacuum. The crystalline compound in 74 % yield (0.22 g, 0.37 mmol) was obtained. Anal. Calc. (%) for C<sub>27</sub>H<sub>32</sub>N<sub>6</sub>SCl<sub>2</sub>Ni: C 54.00, H 5.33, N 18.66, S, 5.33. Found: C 54.11, H 5.41, N 18.75, S 5.45. IR (KBr, cm<sup>-1</sup>): ν(C=S) 1620, ν<sub>as</sub>(NO<sub>3</sub>) 1535, ν<sub>s</sub>(NO<sub>3</sub>) 1267. UV-Vis (CH<sub>3</sub>CN, λ<sub>max</sub>, nm, ε/M<sup>-1</sup>cm<sup>-1</sup>): 288 (927), 518 (232). μ<sub>eff</sub> = 3.46 B.M. at 295 K.

**Synthesis of Ni(pz<sup>Ph,Me</sup>H)<sub>2</sub>(tm<sup>t-Bu</sup>)(NO<sub>3</sub>)<sub>2</sub> (4):** Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.14 g, 0.5 mmol), 1-*tert*-butylimidazole-2-thione (0.08 g, 0.5 mmol) and 3-phenyl-5-methyl-pyrazole (0.16 g, 1.0 mmol) were

Selected Bond Lengths (Å) and Angles (deg.) for Complexes **1** and **4**

<b>1</b>		<b>4</b>			
Bond Distances		Bond Distances		Bond Angles	
Ni(1)—Cl(2)	2.2485(5)	Ni(1)—N(1)	2.0180(16)	N(2)—Ni(1)—S(1)	92.33(5)
Ni(1)—Cl(2')	2.2486(4)	Ni(1)—O(1)	2.1449(14)	N(1)—Ni(1)—O(1)	89.01(6)
Ni(1)—S(1)	2.2898(3)	Ni(1)—O(3)	2.1327(15)	N(1)—Ni(1)—O(3)	160.15(6)
Ni(1)—S(1')	2.2898(3)	Ni(1)—N(2)	2.0637(16)	N(2)—Ni(1)—O(1)	173.82(6)
Bond Angles		Ni(1)—O(2)	2.1069(15)	N(2)—Ni(1)—O(3)	88.36(6)
Cl(2)—Ni(1)—Cl(2')	135.422(17)	Ni(1)—S(1)	2.3930(5)	O(1)—Ni(1)—O(2)	86.05(6)
Cl(2)—Ni(1)—S(1)	96.817(12)	Bond Angles		O(2)—Ni(1)—O(3)	61.33(6)
Cl(2')—Ni(1)—S(1')	96.819(12)	N(1)—Ni(1)—N(2)	94.73(7)	O(2)—Ni(1)—S(1)	159.37(4)
Cl(2)—Ni(1)—S(1')	108.820(11)	N(1)—Ni(1)—O(2)	99.10(6)	O(1)—Ni(1)—O(3)	86.47(6)
Cl(2')—Ni(1)—S(1)	108.816(11)	N(1)—Ni(1)—S(1)	101.37(5)	O(1)—Ni(1)—S(1)	91.74(4)
S(1)—Ni(1)—S(1')	108.856(17)	N(2)—Ni(1)—O(2)	88.50(6)	O(3)—Ni(1)—S(1)	98.09(4)

stirred in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) and CH<sub>3</sub>OH (5 ml) for 2 h. The mixture was filtered over celite and solvent was evaporated to dryness under vacuum. The powdered compound in 82 % yield (0.27 g, 0.41 mmol) was dissolved in CH<sub>3</sub>CN (5 ml) and green crystals were obtained at –20 °C after five days. Anal. Calc. (%) for C<sub>27</sub>H<sub>32</sub>N<sub>8</sub>O<sub>6</sub>SNi: C 49.46, H 4.48, N 17.09. Found (%): C 49.53, H 4.43, N 17.16. IR (KBr, cm<sup>-1</sup>): ν(C=S) 1622, ν<sub>as</sub>(NO<sub>3</sub>) 1532, ν<sub>s</sub>(NO<sub>3</sub>) 1262. UV-Vis (CH<sub>3</sub>CN, λ<sub>max</sub>, nm, ε/M<sup>-1</sup>cm<sup>-1</sup>): 286 (874), 523 (242). μ<sub>eff</sub> = 3.24 B.M. at 295 K.

Elemental analyses were performed using Vario EL III elemental analyzer. The UV-vis spectra were recorded on Perkin-Elmer Lambda 35 UV/vis spectrophotometer. IR spectra were obtained on a Thermo Nicolet Nexus FT-IR spectrometer in KBr. Room temperature magnetic susceptibility measurements were done on a Princeton Applied Research Vibrating Sample Magnetometer Model 155.

The X-ray data collection and processing for **1** and **4** were performed on a Bruker Kappa Apex-II CCD diffractometer with graphite monochromated MoK<sub>α</sub> radiation (λ = 0.71070 Å) at 100 K. Crystal structures were solved by direct methods (Table 1). Structure solution, refinement and data output were carried out using the SHELXTL program [ 20, 21 ]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. Images were created with the DIAMOND program [ 22]. The final values of bond lengths and angles are listed in Table 2. The full crystallographic data including Tables of positional parameters, bond lengths, bond angles and anisotropic thermal displacement parameters were deposited in the form of CIF files at the Cambridge Structural Database (CCDC 690450, 690451) and are available freely upon request citing the deposition number from the web site: [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

The complexes **1** and **2** were synthesized by the reaction of hexahydrate nickel(II) chloride or hexahydrate nickel(II) nitrate with 1-*tert*-butylimidazole-2-thione. Further these nickel salts were treated with 1-*tert*-butylimidazole-2-thione and 3-phenyl-5-methyl-pyrazole to check the structural changes in complexes **3** and **4**. All these complexes were characterized by elemental analysis, IR and UV-vis spectra, magnetic susceptibility and single crystal X-ray diffraction analysis. The complexes **1**–**4** show C=S stretching vibration at 1620±5 cm<sup>-1</sup> suggesting binding with the metal centre. The complexes **2** and **4** show ν<sub>as</sub>(NO<sub>3</sub>) and ν<sub>s</sub>(NO<sub>3</sub>) at 1528–1532 and 1262–1264 cm<sup>-1</sup>, indicating the coordination of nitrate anions. The magnetic moment of 3.91 for complex **1** was consistent with tetrahedral geometry around the metal centre whereas for **3**, the value of 3.46 B.M. would suggest high

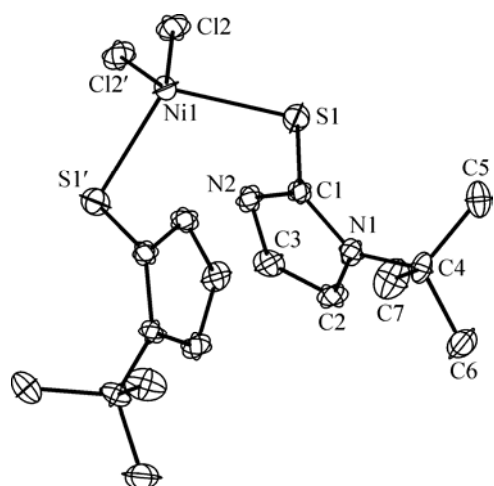


Fig. 1. Thermal ellipsoidal view of complex  $[\text{Ni}(\text{tm}^{\text{t-Bu}})_2\text{Cl}_2]$  **1** with atom labeling at 30% probability level. Hydrogen atoms have been omitted for clarity

spin five coordination and for complex **2** and **4**, this value was 3.20 and 3.24 B.M. indicating octahedral geometry [23]. Although we could not obtain suitable crystals for compound **2** and **3**, the other studies show that the complex **2** may have six coordinated geometry and complex **3** has five coordinated structure. For the preparation of complex **4** various relative amounts of 3-phenyl-5-methyl-pyrazole were used in the reaction mixture but the isolated complex always had 1:1:2 ratio based on the X-ray structure.

#### Molecular and crystal structure of $[\text{Ni}(\text{tm}^{\text{t-Bu}})_2\text{Cl}_2]$

**(1):** The complex **1** crystallizes in monoclinic system with centrosymmetric space group  $C2/c$ . The crystallographic data are listed in Table 1 whereas the most important bond lengths and bond angles are given in Table 2. The thermal ellipsoidal view of complex **1** is shown in Fig. 1 and unit cell packing in Fig. 2. Coordination core of nickel atom in mononuclear complex **1** represents a distorted tetrahedron formed by two sulphur atoms from 1-*tert*-butylimidazole-2-thione and two chloride ions. The nickel-sulphur and nickel-chloride bond distances are 2.2898(3) Å and 2.2485(5) Å respectively, which are in the range of reported for nickel complexes [11]. The geometry around the nickel centre is a distorted tetrahedron with average bond angle of 115.48°.

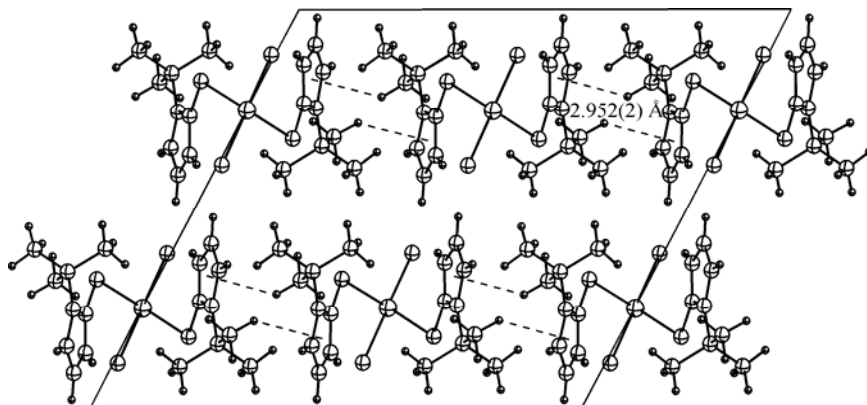


Fig. 2. Non-covalent interaction of complex **1** showing  $\text{CH}_3 \cdots \pi$  and intramolecular  $\text{N}-\text{H} \cdots \text{Cl}$  interactions in the crystal

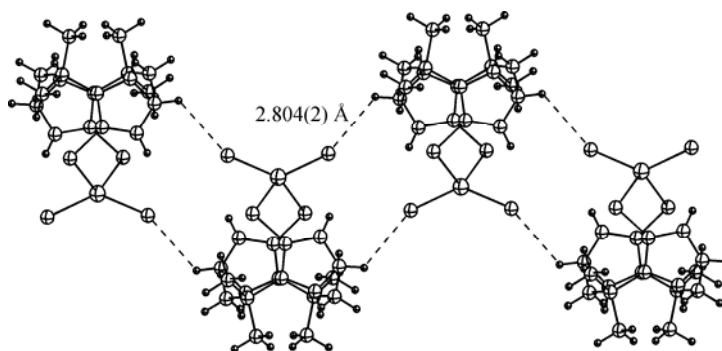


Fig. 3. Zig-zag chain formation in complex **1** due to  $\text{CH} \cdots \text{Cl}$  interactions

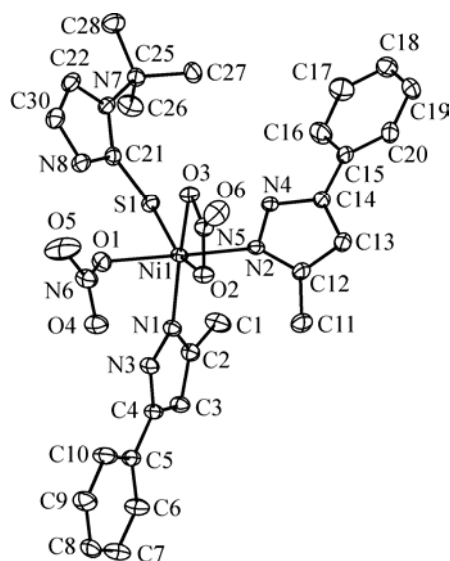


Fig. 4. Thermal ellipsoidal view of complex  $[\text{Ni}(\text{pz}^{\text{Ph,Me}}\text{H})_2(\text{tm}^{\text{t-Bu}})(\text{NO}_3)_2]$  **4** with atom labeling at 50 % probability level. Hydrogen atoms have been omitted for clarity

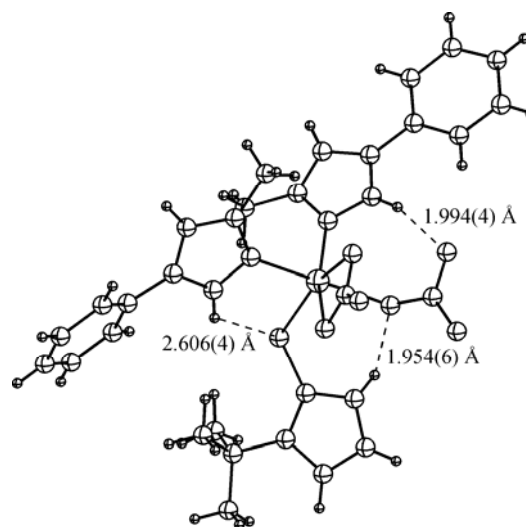


Fig. 5. Intramolecular interactions of complex **4** showing  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{S}$  interactions

Figure 2 shows the presence of  $\text{CH}_3\cdots\pi$  intermolecular interactions ( $2.952(2)$  Å) between one  $\text{CH}_3$  of *tert*-butyl group and  $\pi$ -electrons of imidazole ring and intramolecular  $\text{N}-\text{H}\cdots\text{Cl}$  interaction ( $2.507(12)$  Å) between the hydrogen atom present on nitrogen atom of imidazole and chloride bonded to metal center. Figure 3 shows the formation of zig-zag chain along the *a*-axis due to the presence of non-covalent  $\text{C}-\text{H}\cdots\text{Cl}$  interaction ( $2.804(2)$  Å) between two independent molecules in one chain.

**Molecular and crystal structure of  $[\text{Ni}(\text{pz}^{\text{Ph,Me}}\text{H})_2(\text{tm}^{\text{t-Bu}})(\text{NO}_3)_2]$  (**4**):** The compound **4** crystallizes in triclinic system with space group *P*-1 and its thermal ellipsoidal view is shown in Fig. 4. The nickel centre in this complex is six coordinated with two nitrogen atoms from 3-phenyl-5-methyl-pyrazole, one sulphur atom from 1-*tert*-butylimidazole-2-thione, two oxygen atoms from one nitrate and one oxygen atom from another nitrate ion. Thus it is an ' $\text{N}_2\text{SO}_3$ ' system with distorted octahedral geometry. Here the nitrates are behaving in asymmetric fashion. One of  $\text{Ni}-\text{O}$  distances ( $\text{Ni}(1)-\text{O}(4)$ ,  $3.559$  Å) of monodentately coordinated nitrate anion is too long to count the ligand as bidentate. Another nitrate is bidentate but it also shows difference in the two  $\text{Ni}-\text{O}$  bond lengths,  $2.1069$  and  $2.1449$  Å (Table 2). The bond  $\text{Ni}-\text{S}$  (bond distance  $2.3930(5)$  Å) is coordination bond (as formed by donor-acceptor mechanism) but it does have some character of a covalent bond. The  $\text{Ni}-\text{N}$  bond distances ( $2.0408$  Å) in this complex are well within the range of metal-nitrogen bond distances reported in the literature [ 18, 24–26 ].

Complex **4** is stabilized by two intramolecular  $\text{N}-\text{H}\cdots\text{O}$  interactions {one occurs between hydrogen atom on the nitrogen of pyrazole ring and non-bonded oxygen atom of monodentately coordinated nitrate ion ( $1.994(4)$  Å) and the other occurs between hydrogen atom present on the nitrogen of imidazole ring and bonded oxygen atom of the same anion ( $1.954(6)$  Å)} and one  $\text{N}-\text{H}\cdots\text{S}$  intramolecular interaction between hydrogen atom present on the nitrogen of pyrazole ring and sulphur atom on imidazole (Fig. 5). Due to the involvement of bonded and non-bonded oxygen atoms of both nitrate anions, various other intermolecular interactions, as shown in Fig. 6 and Table 3, occur in the structure [ 27 ]. It is important to mention here that metal complexes with sulphur containing pyrazolylborate were reported in the literature [ 12–16 ] but nickel complex containing both 3-phenyl-5-methyl-pyrazole and 1-*tert*-butylimidazole-2-thione is not available. This complex may be considered as a structural model for nickel-containing superoxide dismutase if one nitrate could be replaced by pyrazole.

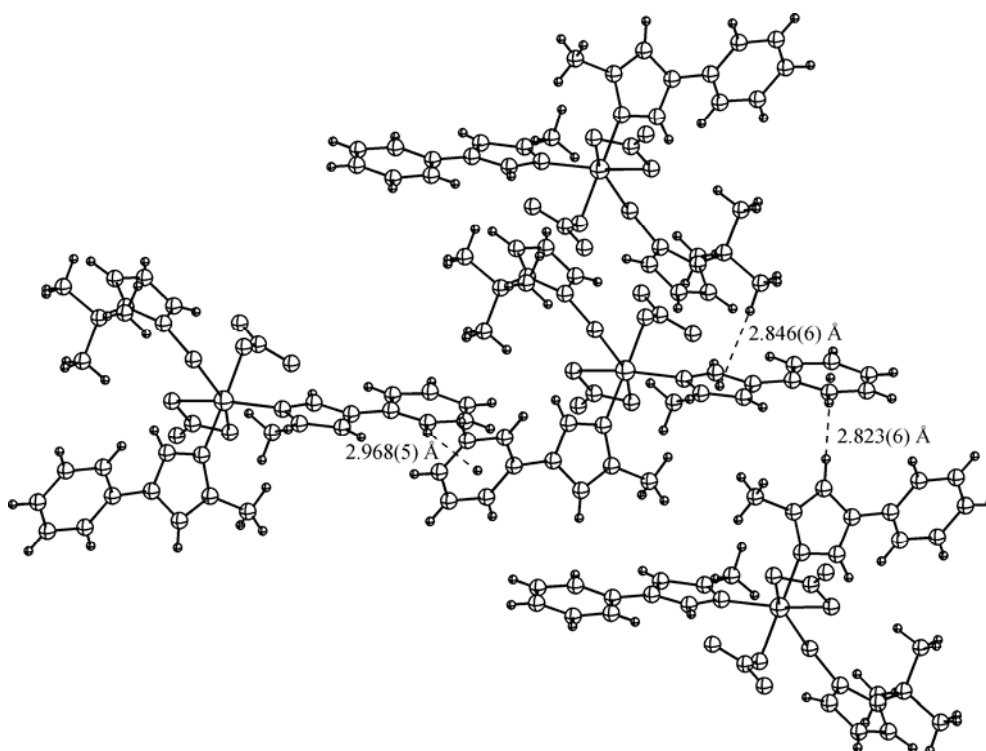


Fig. 6. Intermolecular interactions of complex **4** showing CH $\cdots$  $\pi$  interactions

Table 3

Non-covalent Interactions in Complexes **1** and **4**

D—H $\cdots$ A	D—H	H $\cdots$ A	D $\cdots$ A	DHA
<b>1</b>				
N(2)—H(11) $\cdots$ Cl(2)	0.86	2.507(4)	3.316	156
C(3)—H(3) $\cdots$ Cl(2)	0.93	2.804(2)	3.424(4)	125
C(6)—H(6C) $\cdots$ $\pi$ (tm <sup><i>t</i></sup> -Bu)	0.96	2.952(2)	7.734(3)	104
<b>4</b>				
N(3)—H(2) $\cdots$ O(4)	0.86	1.994(4)	2.824	162
N(8)—H(24) $\cdots$ O(1)	0.86	1.954(6)	2.740	151
N(4)—H(4) $\cdots$ S(1)	0.86	2.606(4)	3.149	122
C(1)—H(1B) $\cdots$ O(6)	0.96	2.328(4)	3.236(4)	158
C(26)—H(26C) $\cdots$ O(1)	0.96	2.551(4)	3.235(7)	128
C(28)—H(28C) $\cdots$ O(5)	0.96	2.625(3)	3.576(4)	171
C(28)—H(28B) $\cdots$ O(5)	0.96	2.667(5)	3.601(6)	164
C(30)—H(23) $\cdots$ O(3)	0.93	2.688(8)	3.316(9)	126
C(17)—H(17) $\cdots$ O(4)	0.93	2.666(5)	3.483(8)	147
C(17)—H(17) $\cdots$ O(2)	0.93	2.524(3)	3.236(5)	134
C(19)—H(19) $\cdots$ O(6)	0.93	2.574(4)	3.363(6)	143
C(28)—H(28A) $\cdots$ $\pi$ (pzofpz <sup>Ph,Me</sup> )	0.96	2.846(6)	3.770(8)	162
C(13)—H(13) $\cdots$ $\pi$ (Phofpz <sup>Ph,Me</sup> )	0.93	2.823(6)	3.681(7)	154
C(6)—H(6) $\cdots$ $\pi$ (Phofpz <sup>Ph,Me</sup> )	0.93	2.968(5)	3.776(7)	146

## CONCLUSIONS

In conclusion, we have prepared several nickel complexes having 1-*tert*-butylimidazole-2-thione and 3-phenyl-5-methyl-pyrazole as ligands. Due to different binding sites of 1-*tert*-butylimidazole-2-thione and 3-phenyl-5-methyl-pyrazole, these complexes differ in their molecular structure. The complex **1** exhibits tetrahedral coordination environment, and shows zig-zag chain formation due to the presence of C—H...Cl interaction between bonded chloride and hydrogen atom present on the imidazole ring. Complex **4** is an example where bonded nitrate anions are coordinated in both monodentate and bidentate fashion. Along with the presence of two nitrate anions, complex **4** shows various inter and intramolecular interactions in its crystal packing.

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