

# Synthesis, structural characterization, electrochemical studies and DFT calculations on nickel(II) complexes of *N*-picolinoyl-*N*'benzothioylhydrazide and 5-(pyridine-4-yl)-2H-1,2,4-triazole-3thione

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Abstract Two Ni(II) complexes, [Ni(pbth)<sub>2</sub>] and [Ni(ptt)<sub>2</sub>- $(en)_2$ {Hpbth = N-picolinoyl-N'-benzothioylhydrazide,  $Hptt = 5-(pyridine-4-yl)-2H-1,2,4-triazole-3-thione \}$  have been synthesized and characterized by physico-chemical and spectroscopic methods. [Ni(pbth)<sub>2</sub>] contains a pair of N-picolinoyl-N'-benzothioylhydrazide ligands coordinated via their thione sulfur, pyridyl nitrogen and hydrazinic nitrogen atoms, forming two  $C_2N_2N_i$  and two  $CSN_2N_i$  five-membered chelate rings. The intermediate compound 1-isonicotinoyl-3thiosemicarbazide is converted to 5-(pyridine-4-yl)-2H-1,2,4triazole-3-thione in the presence of ethanolic NaOH, giving the complex  $[Ni(ptt)_2(en)_2]$  in which the ptt ligands coordinate through their triazole ring nitrogen atoms, while four more nitrogens from two ethylenediamine ligands complete the octahedral structure. The crystal structures of the complexes involve various types of intermolecular extended hydrogen bonds, forming supramolecular frameworks. Cyclic voltammetry studies of both complexes show quasi-reversible redox behavior. Density Functional Theory electronic structure calculations corroborate our experimental findings.

# Introduction

The coordination chemistry of nitrogen-sulfur ligands is of interest since their complexes can possess semiconducting behavior, molecular magnetism, optoelectronic and

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<sup>2</sup> Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA electrochemical properties [1–3]. Known types of nitrogen– sulfur ligands include thiohydrazides, thiosemicarbazides, thiosemicarbozones, N-acyl-N'-thioaroylhydrazides, N and S substituted dithiocarbazates, N-acyl-N'-carbodithioic acid esters, and 1,2,4-triazoles. In their deprotonated forms, Npicolinoyl-N'-benzothioylhydrazide (Hpbth) and 5-(pyridine-4-yl)-2H-1,2,4-triazole-3-thione (Hptt) can bind to nickel through either sulfur, or nitrogen, or both. After thiosemicarbazides, the N'-thioaroyl derivatives of acyl hydrazines are the next higher homologues of biologically important compounds which display beneficial biological activities, including antitumor, antibacterial, antiviral and antimalarial activities [4, 5]. The biological activities of these compounds are considered to be due to the presence of the HNCS moiety, which can form chelates with metals. Due to the presence of O, N, S potential donor sites, thiocarbohydrazide derivatives are interesting ligands that can generate mononuclear, dinuclear and even tetranuclear complexes which provide a new dimension in supramolecular chemistry [6, 7]. In recent years, the selfassembly of heterocyclic ligands such as substituted triazoles and their derivatives has become one of the most efficient and widely utilized approaches to the construction of inorganic coordination supramolecular architectures. Such architectures exhibit potential applications in catalysis, electrical conductivity, molecular-based magnets, ion exchange, fluorescent and nonlinear optical materials and host-guest chemistry [8, 9]. 1,2,4-triazole and its derivatives are very interesting for the preparation of polynuclear complexes because they can coordinate to a metal in different ways, depending on the position and nature of the substituents [10]. A number of functionalized triazoles are readily accessible; these include heterocyclic  $\pi$ -conjugated systems with good coordination abilities to metal centers and the capability to exhibit luminescence or other properties. These ligands have a variety of bridging modes with extra potential donor sites provided by the functional groups substituted on the triazole rings. Their nitrogen atoms can also serve as hydrogen bond acceptors, while their aromatic rings can participate in  $\pi$ - $\pi$  stacking, leading to secondary noncovalent interactions in metal-triazole complexes [11].

In view of the above, much research on 1,2,4-triazole and its derivatives has been carried out and a large number of complexes with interesting structures and properties have been reported [12, 13]. Herein, we report the synthesis of 5-(pyridine-4-yl)-2H-1,2,4-triazole-3-thione through the intramolecular cyclization of a 1,4-disubstituted thiosemicarbazide. A Ni(II) complex of this ligand is described, together with the synthesis and characterization of a Ni(II) complex of *N*-picolinoyl-*N*'-benzothioylhydrazide.

#### **Experimental**

#### Chemicals and starting materials

Isonicotinoyl chloride hydrochloride, phenyl isothiocyanate (Sigma Aldrich), hydrazine hydrate, thiosemicarbazide, metal salts, ethylenediamine (en) (BDH Chemicals) were used as received. All the synthetic manipulations were carried out in open air at room temperature. The solvents were distilled before use.

#### **Physical measurements**

Carbon, hydrogen, nitrogen and sulfur contents were estimated on a CHN Model CE-440 Analyzer and on an Elementar Vario EL III Carlo Erba 1108 instrument. Electronic spectra were recorded on a Shimadzu UV-1700 Pharmaspec spectrometer. Room-temperature magnetic susceptibility measurements were made on a Cahn-Faraday electrobalance using cobalt mercury tetrathiocyanate calibrant. IR spectra were recorded in the as  $4000-400 \text{ cm}^{-1}$  region as KBr pellets on a Varian Excalibur 3100 FTIR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in DMSO- $d_6$  on a JEOL AL300 FTNMR spectrometer using TMS as internal reference. Electrochemical studies were performed on a Metrohm (Netherlands) Instrument (Autolab PGSTAT204) potentiostat/galvanostat using NOVA 1.11 software. A three electrode, one compartment cell with solid platinum electrode as the working electrode, platinum wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode were used. All electrochemical studies were carried out at room temperature under nitrogen.

#### Synthesis of N-picolinoyl-N'-benzothioylhydrazide

The preparation and characterization of *N*-picolinoyl-*N*'-benzothioylhydrazide (Hpbth) are described elsewhere [14].

# Synthesis of [Ni(pbth)<sub>2</sub>]

A methanol-acetonitrile solution (20 ml, 50:50 v/v) of Npicolinoyl-N'-benzothioylhydrazide (0.25 g, 1 mmol) was added slowly to a methanol (10 ml) solution of NiCl<sub>2</sub>.6-H<sub>2</sub>O (0.06 g, 0.5 mmol), and the mixture was stirred for 2 h. The resulting precipitate was filtered off, washed with an ethanol-water mixture (50:50 v/v) and suspended in methanol to which a hot methanol solution of pyridine (5 drops) was added. The mixture was then stirred for 3 h at room temperature. The clear brown solution thus obtained was filtered off and kept for crystallization. Red-brown crystals suitable for X-ray analyses were obtained by slow evaporation over a period of 20 days. Yield: 66%; m.p. 236 °C. Anal. Found: C, 54.7; H, 3.6; N, 14.7; S, 11.3%. Calc. for C<sub>26</sub>H<sub>20</sub>NiN<sub>6</sub>S<sub>2</sub>O<sub>2</sub> (571.31): C, 54.6; H, 3.5; N, 14.7; S, 11.2%. IR (KBr, cm<sup>-1</sup>): v(N-H) 3404 s (Calc. 3478); v(C=O) 1623 m (Calc. 1702); v(N-N) 1143 m (Calc. 1188); v(C=S) 956 w (Calc. 960); (Ni-N) 605 m (Calc. 636); (Ni-S) 424 m (Calc. 362).

# Synthesis of 5-(pyridine-4-yl)-2H-1,2,4-triazole-3-thione

1-Isonicotinoyl-3-thiosemicarbazide was prepared by refluxing methanolic solutions of isonicotinovl chloride hydrochloride (1.78 g, 10 mmol) and thiosemicarbazide (0.75 g, 10 mmol) for 5 h. The reaction mixture was brought to room temperature, and the white solid so obtained was filtered off, washed with cold water and recrystallized from an EtOH-H<sub>2</sub>O mixture (20%, v/v). Yield: 78%. 5-(Pyridine-4-yl)-2H-1,2,4-triazole-3-thione was synthesized by dissolving freshly prepared 1-isonicotinoyl-3-thiosemicarbazide (1.176 g, 6 mmol) in aqueous NaOH (10%, 10 ml) and refluxing for 3 h. The solution was cooled in ice and acidified with dil. HCl. The white precipitate so obtained was filtered off, washed with water, air-dried and recrystallized from ethanol. Yield: 83%; m.p. 212 °C. Found: C, 47.3; H, 3.4; N, 31.6; S, 18.1%. Calc. for C<sub>7</sub>H<sub>6</sub>N<sub>4</sub>S (178.03): C, 47.2; H, 3.4; N, 31.5; S, 18.0%. IR (cm<sup>-1</sup>, KBr): v(N–H) 3210 m, 3112 m; v(C=N) 1548 s;



Scheme 1 Synthesis of Hpbth and its complex [Ni(pbth)<sub>2</sub>]





ν(N–N) 1069 w; ν(C=S) 1003 w. <sup>1</sup>H NMR (DMSO- $d_6$ ; δ ppm): 10.63, 9.89 (s,2H, NH), 6.48–7.86 (m, aromatic protons). <sup>13</sup>C NMR (DMSO- $d_6$ ; δ ppm): 168.78 (C=S), 161.03 (C=N), 117.21–134.32 (aromatic carbons).

## Synthesis of [Ni(ptt)<sub>2</sub>(en)<sub>2</sub>]

A methanolic solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.06 g, 0.5 mmol) was added to a methanolic solution of Hptt (0.18 g, 1 mmol), and the mixture was stirred for 1 h. The brown precipitate was filtered off, washed with an ethanol–water mixture (50:50) and suspended in methanol to which a methanol solution of (en) (2 drops) was added. The mixture was then stirred for 3 h. The resulting brown solution was filtered and kept for crystallization. Brown crystals of the complex suitable for X-ray analyses were obtained by slow evaporation of the methanol solution over a period of 20 days. Yield: 58%; m.p. 228 °C. Found: C, 40.6; H, 4.9; N, 31.6; S, 12.1%. Calc. for  $C_{18}H_{26}N_{12}NiS_2$  (533.34): C,

40.5; H, 4.9; N, 31.5; S, 12.0%. IR (cm<sup>-1</sup>, KBr): v(N–H) 3103 w (Calc. 3244); v(C=N) 1594 s (Calc. 1572); v(N–N) 1073 m (Calc. 1082); v(C=S) 970 s (Calc. 1028), v(Ni–N) 523 s (Calc. 490).

#### **Crystal structure determination**

The X-ray data collections for the complexes were performed with an Oxford Diffraction Gemini diffractometer equipped with CrysAlis Pro., using a graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation source at 293 K. A multi-scan absorption correction was applied to the X-ray data collection. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least squares on  $F^2$  (SHELXL-97) using anisotropic displacement parameters for all nonhydrogen atoms. All of the hydrogen atoms were included in the refinement at geometrically ideal positions and refined with the riding model [15]. The MERCURY package and ORTEP-3 for Windows



Fig. 1 Cyclic voltammograms of complexes: a [Ni(pbth)<sub>2</sub>] and b [Ni(ptt)<sub>2</sub>(en)<sub>2</sub>]



**Fig. 2** ORTEP diagram of [Ni(pbth)<sub>2</sub>] at 30% ellipsoids probability level. Hydrogen atoms are omitted for clarity

program were used for analysis of the structures and drawing of the figures [16, 17].

#### Quantum chemical calculations

Density Functional Theory (DFT) calculations were performed using the B3LYP functional [18]. The 6-31G\*\* basis set was used for all atoms except Ni, for which the LanL2DZ basis set with an effective core pseudo-potential [19] was used. All geometry optimizations and frequency calculations (to verify genuine minimum energy structures) were performed using the Gaussian 09 program package [20].

### **Results and discussion**

Reactions of *N*-picolinoyl-*N*'-benzothioylhydrazide and 5-(pyridine-4-yl)-2H-1,2,4-triazole-3-thione with NiCl<sub>2</sub>-6H<sub>2</sub>O, upon treatment of the precipitate with a few drops of py or en, yielded complexes [Ni(pbth)<sub>2</sub>] and [Ni(ptt)<sub>2</sub>(-en)<sub>2</sub>], respectively, which are stable toward air and moisture. The intermediate 1-isonicotinoyl-3-thiosemicarbazide was prepared by the reaction of isonicotinoyl chloride with thiosemicarbazide, which on refluxing with ethanolic NaOH yielded 5-(pyridine-4-yl)-2H-1,2,4-triazole-3-thione via a cyclization reaction. [Ni(pbth)<sub>2</sub>] and [Ni(ptt)<sub>2</sub>(en)<sub>2</sub>] melt at 236 and 228 °C, respectively. Schemes 1 and 2 depict the formation of ligands and their complexes. The complexes are insoluble in methanol and ethanol but are soluble in DMF and DMSO.

#### **IR** spectra

The IR spectrum of free Hpbth shows absorptions due to the stretching modes of NH (3436); C=O (1661); C=S (998) and N–N (1175 cm<sup>-1</sup>) [14]. The FTIR spectrum of complex [Ni(pbth)<sub>2</sub>] does not include a v(NH) band; together with two new bands assigned to v(Ni–N) and v(Ni–S) at 605 and 424 cm<sup>-1</sup>, respectively, this suggests bonding of Ni(II) with a hydrazine nitrogen [21]. The v(C=S) band suffers a negative shift of 42 cm<sup>-1</sup>, suggesting that pbth is acting as uninegative tridentate ligand, bonding through a thione sulfur. This chelating mode is confirmed by X-ray crystallography. The IR spectrum of free 5(pyridine-4-yl)-2H-1,2,4-triazole-3-thione shows two

**Table 1** Crystallographic data, structure solution and refinement for [Ni(pbth)<sub>2</sub>] (1) and [Ni(ptt)<sub>2</sub>(en)<sub>2</sub>] (2)

Parameters	$[Ni(pbth)_2]$ (1)	$[Ni(ptt)_2(en)_2]$ (2)
Empirical formula	C <sub>26</sub> H <sub>20</sub> N <sub>6</sub> NiO <sub>2</sub> S <sub>2</sub>	C <sub>18</sub> H <sub>26</sub> N <sub>12</sub> NiS <sub>2</sub>
Formula weight	571.35	533.34
T (K)	173 (2)	293(2)
Λ (Mo Kα) (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C 2/c	P 21/n
a (Å)	24.178(4)	10.9114(5)
b (Å)	8.9617(6)	10.2007(4)
c (Å)	15.381(3)	11.9784(6)
β (°)	129.49(3)	114.021(6)
V (Å <sup>3</sup> )	2572.1(7)	1217.78(11)
Z	4	2
$D_{\rm calc} \ ({\rm mg \ m}^{-3})$	1.475	1.454
$\mu (mm^{-1})$	0.953	1.001
F(000)	1176	556
Crystal size (mm <sup>3</sup> )	$0.28 \times 0.26 \times 0.23$	$0.28 \times 0.27 \times 0.24$
$\theta$ range (°)	3.42-29.08	3.72-29.16
Index ranges	$-32 \le h \le 32$	$-13 \le h \le 14$
	$-12 \le k \le 5$	$-7 \le k \le 13$
	$-19 \le l \le 18$	$-10 \le l \le 16$
Reflections collected	2503	3280
Independent reflections	1898	2114
Data/restraints/parameters	2503/72/167	2756/0/151
Goodness-of-fit on F <sup>2</sup>	1.027	0.933
$R_1^a, wR_2^b [(I > 2\sigma(I)]]$	0.0479, 0.1124	0.0453, 0.1055
R <sub>1</sub> <sup>a</sup> , wR <sub>2</sub> <sup>b</sup> (all data)	0.0706, 0.1302	0.0635, 0.1254
Largest diff. peak/hole (e $Å^{-3}$ )	0.595, -0.817	0.778, -0.904

<sup>a</sup>  $R_1 = \Sigma ||F_o| - |Fc||\Sigma|F_o|,$ 

<sup>b</sup>  $R_2 = [\Sigma w (|F_o^2| - |F_c^2|)^2 / \Sigma w |F_o^2|^2]^1$ 

absorption bands at 3210 and 1003 cm<sup>-1</sup>, assigned to the NH and C=S stretching modes, respectively. The IR spectrum of  $[Ni(ptt)_2(en)_2]$  does not show a v(N-H) band, due to the loss of hydrogen from the triazole ring, while a small positive shift in v(N-N) indicates bonding of the triazole nitrogen to the metal. The spectrum of this complex shows a new band at 3103 cm<sup>-1</sup> assigned to the NH stretching vibrations of en, which occur at a lower frequency than encountered in free ethylenediamine [22]. A new band at 523 cm<sup>-1</sup> assigned to v(Ni–N) suggests the chelating en ligands.  $[Ni(ptt)_2(en)_2]$  shows a small negative shift in v(C=S) as compared to the free ligand; this suggests that the exocyclic sulfur is not coordinating to the metal, rather the small negative shift can be attributed to the involvement of sulfur in hydrogen bonding. The calculated values for the v(N-H), v(C=O), v(N-N), v(C=S) vibrations are in good agreement with the experimental data.

# Electronic spectra, magnetic moments and electrochemical behavior

Magnetic moment values of 2.84 and 2.90 BM for the Ni(II) complexes [Ni(pbth)<sub>2</sub>] and [Ni(ptt)<sub>2</sub>(en)<sub>2</sub>], respectively, indicate the presence of two unpaired electrons. The UV–Vis absorption spectra each show two bands, at 781 and 515 nm for [Ni(pbth)<sub>2</sub>] and 779 and 514 nm for [Ni(ptt)<sub>2</sub>(en)<sub>2</sub>], assigned to the  ${}^{3}A_{2}g \rightarrow {}^{3}T_{2}g(F)$  (v<sub>1</sub>) and  ${}^{3}T_{1}g(F)$  (v<sub>2</sub>) transitions, respectively, suggesting distorted octahedral geometries for both complexes. Other high energy bands occurring in the region of 320–285 nm may be assigned to intraligand/charge transfer transitions [23].

The electrochemical behavior of both complexes under cyclic voltammetry is depicted in Fig. 1. The cyclic voltammograms were obtained using SCE (Hg/Hg<sub>2</sub>Cl<sub>2</sub>) with 0.1 M KCl as supporting electrolyte in the potential

**Table 2** Selected bond lengths(Å) and bond angles (°) forcomplexes

Bond lengths (Å)		Bond angles (°)			
	Exp.	Cal.		Exp.	Cal.
[Ni(pbth) <sub>2</sub> ]	(1)				
Ni-N2	1.990 (3)	1.826	N2-Ni-N2	178.71 (15) 2_554	178.29
Ni-N2	1.990 (3) 2_554	1.826	N2-Ni-N1	103.36 (11) 2_554	103.63
Ni-N1	2.124 (3)	2.181	N2-Ni-N1	77.61 (10)	75.07
Ni-N1	2.124 (3) 2_554	2.181	N1-Ni-N1	84.88 (14) 2_554	84.07
Ni-S1	2.4547 (10)	2.471	N2-Ni-S1	97.99 (9) 2_554	82.61
Ni-S1	2.4547 (10) 2_554	2.471	N1-Ni-S1	95.65 (8) 2_554	91.47
S1-C7	1.680 (3)	1.856	N2-Ni-S1	81.11 (8)	82.61
O1-C6	1.243 (4)	1.242	N1-Ni-S1	158.22 (8)	155.44
N1-C1	1.333 (5)	1.334	S1-Ni-S1	91.80 (5) 2_554	101.97
[Ni(ptt)2(en)	) <sub>2</sub> ] ( <b>2</b> )				
Ni–N5	2.093 (2) 3	1.960	N5-Ni-N5	180.00 (15) 3	180.00
Ni–N5	2.093 (2)	1.960	N5-Ni-N6	97.27 (10) 3	86.71
Ni-N6	2.103 (3)	1.960	N5-Ni-N6	82.73 (10)	86.71
Ni-N6	2.103 (3) 3	1.960	N6-Ni-N6	180.00(17) 3	180.00
Ni–N1	2.117 (2)	2.632	N5-Ni-N1	89.62 (9) 3	87.18
Ni–N1	2.117 (2) 3	2.632	N5-Ni-N1	90.38 (9)	87.18
S1-C7	1.682 (3)	1.730	N6-Ni-N1	90.41 (10) 3	87.76
N3-C7	1.379 (4)	1.375	N6-Ni-N1	90.41 (10) 3	87.76
N3-C6	1.347 (4)	1.375	N1-Ni-N1	180.00 (15)	180.00



Fig. 3 N-H…O hydrogen bonding in complex  $[Ni(pbth)_2]$  leading to a supramolecular architecture

range of 0.05–0.7 V with a scan rate of 100 mVs<sup>-1</sup>. Both complexes show quasi-reversible redox behavior. [Ni(pbth)<sub>2</sub>] exhibits anodic and cathodic peak potentials at 0.419 and 0.237 V, while [Ni(ptt)<sub>2</sub>(en)<sub>2</sub>] shows anodic and cathodic peak potentials at 0.480 and 0.250 V, respectively. The separations between the anodic and cathodic peak potentials are ( $\Delta E_p = E_{pa}-E_{pc}$ ) 0.182 and 0.230 V, respectively, suggesting a quasi-reversible redox process Table 3 Intermolecular hydrogen bond and weak intermolecular parameters [Å and °] in complex  $[Ni(pbth)_2]$  (1)

D–H <sup>…</sup> A	d (D-H)	d (H <sup></sup> A)	d (DA)	<(DHA)
N3–H3A <sup>…</sup> O1	0.860	1.911	2.766	172.78
C12-H12O1	0.931	2.664	3.530	155.19
N3-H3A01	0.860	2.490	2.746	98.04
C4-H4O1	0.931	2.572	2.836	96.72

assignable to the Ni(II)/Ni(III) couple with redox potentials of  $E = (E_{pa} + E_{pc})/2 = 0.328$  and 0.365 V, respectively [24]. These peak separations are somewhat larger than that expected for a one-electron process, suggesting that the quasi-reversible redox process is coupled with some chemical reaction.

# Crystal structure of [Ni(pbth)<sub>2</sub>]

Figure 2 shows an ORTEP diagram of  $[Ni(pbth)_2]$ , together with the atom numbering scheme. The complex contains a pair of *N*-picolinoyl-*N'*-benzothioylhydrazide ligands coordinated to Ni(II). The crystallographic data and structural refinement details are given in Table 1, and selected bond distances and bond angles are compiled in Table 2. The C=O bond length of 1.243(4) Å indicates C3





double-bond character; this group remains uncoordinated, but is involved in the supramolecular architecture through hydrogen bonding. The metal center is coordinated in an N<sub>4</sub>S<sub>2</sub> manner by two uninegative ligands using pairs of pyridine-N, hydrazine-N and thione-S atoms, forming two C<sub>2</sub>N<sub>2</sub>Ni and two CSN<sub>2</sub>Ni five-membered chelate rings. The carbon sulfur bond distances are equal (1.680 (4) Å) and suggest an intermediate character between a single and double bond [25]. Additionally, the N-N distance of 1.382(4) Å in the chelate ring is also intermediate between single- and double-bond lengths, indicating delocalization within the chelate ring [26]. The angles around the Ni(II) [N(1)-Ni-N(2) = 77.61]center, (10),N(1)-Ni-N(2) = 103.36(11), N(2)-Ni-S(1) = 97.99(9), N(2)-Ni-S(1) = 81.11(8), N] (Table 2) indicate some distortion from an ideal octahedral geometry. The Ni-N, C=O, and C=S bond lengths are in good agreement with values for

similar complexes reported in the literature [27]. The chelate rings and the pyridine ring lie nearly in the same plane, such that the pyridine ring makes an extended coplanar system with the two chelate rings. The average bond lengths in  $[Ni(pbth)_2]$  are: Ni-N2 = 1.990(3), N2-N3 = 1.382(4), S1-C7 = 1.680(3), Ni-S1 = 2.454(10),N3-C7 = 1.316(4) Å for the chelate ring Ni/S1/C7/N2/N3 Ni-N2 = 1.990(3),N2-C6 = 1.317(4),and C5-C6 = 1.490(5) Å, C5-N1 = 1.349(4), Ni-N1 = 2.124(3)Å for the chelate ring Ni/N1/N2/C5/C6, again suggesting considerable delocalization of charge within the chelate ring. The pyridine and phenyl rings are nearly perpendicular to each other, with a dihedral angle of 79.05°. The crystal structure of the complex exhibits N-H...O intermolecular hydrogen bonding between the carbonyl oxygen and hydrazinic hydrogen (Fig. 3) of adjacent ligands, leading to a supramolecular architecture (Table 3).



Fig. 6 Frontier molecular orbitals of  $[Ni(pbth)_2]$  (1) and  $[Ni(ptt)_2(en)_2]$  (2)

Molecule	Energy (ev)			
	НОМО	LUMO	Energy gap	
[Ni(pbth) <sub>2</sub> ] (1)	-4.6939	-2.0288	2.6650	
[Ni(ptt) <sub>2</sub> (en) <sub>2</sub> ] (2)	-5.1119	-1.7385	3.3733	

## Crystal structure of [Ni(ptt)<sub>2</sub>(en)<sub>2</sub>]

Figure 4 shows an ORTEP diagram of  $[Ni(ptt)_2(en)_2]$ , together with the atom numbering scheme. The Ni(II) center is coordinated by six nitrogen atoms; two from each of the monodeprotonated triazole ligands, plus four from two en ligands forming two five-membered chelate rings. The crystallographic data and structural refinement details are given in Table 1, and selected bond distances and angles are compiled in Table 2. The monomeric unit of  $[Ni(ptt)_2(en)_2]$  possesses a centrosymmetric nickel atom at the inversion center and the anionic ptt<sup>-</sup> ligand adopts the thione form. The coordination environment around nickel is provided by two mutually *trans*-ptt<sup>-</sup> ligands, each bonded through a triazole ring nitrogen, plus two ethylenediamine ligands. The Ni-N (triazole) bond length is 2.117 (2) Å, while the en ligands have an Ni-N(6) distance of 2.103(3) and Ni–N(5) distance of 2.093(2) Å (Table 2). The complex shows two five-membered chelate rings,  $C_2N_2N_1$ , with a bite angle of  $82.73(10)^\circ$ , with relatively minor deviation from octahedral geometry. The chelate rings are intermediate between single- and double-bond lengths, such that the average bond lengths Ni-N6 = 2.103(3), N6-C9 = 1.473(4), C9-C10 = 1.507(5),C10-N5 = 1.473(4) and Ni-N5 = 2.093(2) Å, suggesting considerable delocalization of charge [26]. The phenyl and triazole rings are nearly co-planar, with a dihedral angle of  $9.29^{\circ}$ . The two five-membered chelate rings of the en ligands have bite angles of  $82.73(10)^{\circ}$  and  $97.27(10)^{\circ}$ , again showing slight distortions from ideal octahedral geometry. The geometry and bonding parameters within the en ligands agree with those of other ethylenediamine complexes [28, 29]. Weak intermolecular N–H…N hydrogen bonding between NH groups of the en ligands and pyridine nitrogens contribute to the formation of a supramolecular architecture (Fig. 5).

#### **DFT** calculations

Input geometries of the complexes for the DFT calculations were generated from the single-crystal X-ray data. Slight disagreements in the observed and calculated bond lengths,  $C7-S1 = 1.680 (1.856)_{calc}$ ;  $Ni-N2 = 1.990 (1.826)_{calc}$  for  $[Ni(pbt)_2]$  (1) and  $Ni-N1 = 2.117 (2.632)_{calc}$ ;  $S1-C7 = 1.682 (1.730)_{calc}$  for  $[Ni(ppt)_2(en)_2]$  (2) may be due to the fact that the DFT calculations are for an isolated molecule in the gas phase, while the X-ray crystallographic data were obtained from the crystal lattice. Nevertheless, there is generally good agreement between the geometrical parameters obtained by X-ray crystallography to those generated by the DFT method (Table 2).

Analysis of the wave function indicates that the electronic absorption is mainly described by a one-electron excitation from the HOMO to the LUMO [30]. Figure 6 shows the shapes and energies of the HOMO and LUMO for both complexes. For  $[Ni(pbth)_2]$ , the HOMO and LUMO are both centered on the metal and its surrounding donor atoms, particularly the two sulfur atoms. In contrast, the HOMO of the  $[Ni(ptt)_2(en)_2]$  is located mainly on the ptt ligands, while the LUMO is again centered on the metal and its surrounding donor atoms. The HOMO–LUMO energy gaps for  $[Ni(pbth)_2]$  and  $[Ni(ptt)_2(en)_2]$  are 2.665 and 3.373 eV, respectively (Table 4). Since the energy gap is smaller for  $[Ni(pbth)_2]$  than  $[Ni(ptt)_2(en)_2]$ ,  $[Ni(pbth)_2]$  would be a better target for photophysical studies and electronics applications [31, 32].

#### Conclusion

In conclusion, we have reported the synthesis, structural characterization and electrochemical studies of two new octahedral Ni(II) complexes. Electrochemical studies showed that both complexes show quasi-reversible redox behavior, assigned to the nickel(II)/nickel(III) couple. The smaller band gap of [Ni(pbth)<sub>2</sub>] suggests that it would be more promising for electronics applications.

#### Supplementary material

CCDC 1006463 and 1006464 contain the supplementary crystallographic data for  $[Ni(pbth)_2]$  and  $[Ni(ptt)_2(en)_2]$ . These data can be obtained free of charge via http://www. ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 IEZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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