



Synthesis and characterization of [chloro{2(1H)-pyridinethione-S}{tris(pyridin-2-ylthiolato)methyl-C,N,N',N''}]nickel(II), [Ni(TPTM)(SPyH)Cl]

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ABSTRACT

The compound, [chloro{2(1H)-pyridinethione-S}{tris(pyridin-2-ylthiolato)methyl-C,N,N',N''}]nickel(II), [Ni(TPTM)(SPyH)Cl], was isolated from the reaction between NiCl₂ · 6H₂O and tris(pyridin-2-ylthio) methane in aqueous EtOH. X-ray crystallography at 120 K revealed an octahedral arrangement about Ni with a tetradentate tris(pyridin-2-ylthio)methyl-C,N,N,N ligand, a monodentate 2(1H)-pyridinethione-S ligand and a chloride. The 2(1H)-pyridinethione-S ligand was derived from tris(pyridin-2-ylthio)methane probably via an acid catalysed hydrolysis reaction. Intramolecular N–H–Cl and C–H–Cl interactions help to cement the molecular structure. Weak C–H–Cl and C–H–S hydrogen bonding interactions link molecules of [Ni(TPTM)(SPyH)Cl] into a 3D array. EPR and UV spectra, and Hartree–Fock theoretical calculations are reported.

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1. Introduction

In recent years, there has been an upsurge in interest in the coordination chemistry of heterocyclic thiones and thioethers containing pyridyl groups. Such ligands are of interest due to the various possibilities for interaction with metal centers: furthermore many of these ligands, and their metal-containing derivatives, have pharmacological applications [1]. 2-Pyridine-thiol (or its tautomer, 2-(1H)-pyridinethione), see Fig. 1, is of particular interest since it is one of the simplest of such derivatives, which can bind metal centres in η^1 , η^2 or η^3 fashions. It also can be used as a precursor for more elaborate ligands, such as bis- and tris-(2-mercaptopyridyl)methane, (2-PyS)₂CH₂ (BPTM-H), and (2-PyS)₃CH (TPTM-H), respectively, see Fig. 1, previously reported and characterised by our group [2]. Other interesting ligands of this type include bis-{2-mercapto-[3,6-(*t*-butyldimethylsilyl)pyridyl]}methane [3] and some mercapto-pyridyl-based-cyclophanes [4].

Very recently, copper(II) complexes of [TPTM][−], namely, [Cu(TPTM)(CH₃CN)]PF₆ and [Cu(TPTM)(X)] (X = F, Cl, Br, and I),

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were isolated, from reactions of TPTM-H [5]. Subsequently, the interesting Cu(III) complex, [Cu(TPTM)(Cl)]PF₆ was obtained via oxidation of [Cu(TPTM)(Cl)] [6]. In all these copper complexes, the TPTM ligand was shown by X-ray crystallography to be acting as a tetradentate, C,N,N,N-ligand. Also reported have been 1:1 [TPTM–H] complexes with R₃SnCl and R₂SnCl₂, for which IR evidence indicated Sn–N coordination in the solid state, but as no crystal structures were determined, the precise coordination modes are unknown. In solution, dissociations of the 1:1 complexes were indicated by the δ^{119} Sn NMR experiments [7]. These recent publications have prompted us to report the synthesis and characterisation of the Ni(II) complex, [chloro{2(1H)-pyridinethione-S}{tris(pyridin-2-ylthiolato)methyl-C,N,N',N''}]nickel(II), [Ni(TPTM)(SPyH)Cl] (1), obtained from the reaction of NiCl₂ · 6(H₂O) with TPTM-H. In addition to a crystal structure determination, EPR spectrum and Hartree–Fock theoretical calculations have been carried out (see Fig. 2).

2. Experimental

2.1. General

The C, N, and H analyses were determined on a Perkin–Elmer, CHN – 2400. Infrared spectra were recorded 4000–370 cm^{−1} on a Perkin–Elmer Spectrum GX FT-IR System. The solid-state elec-

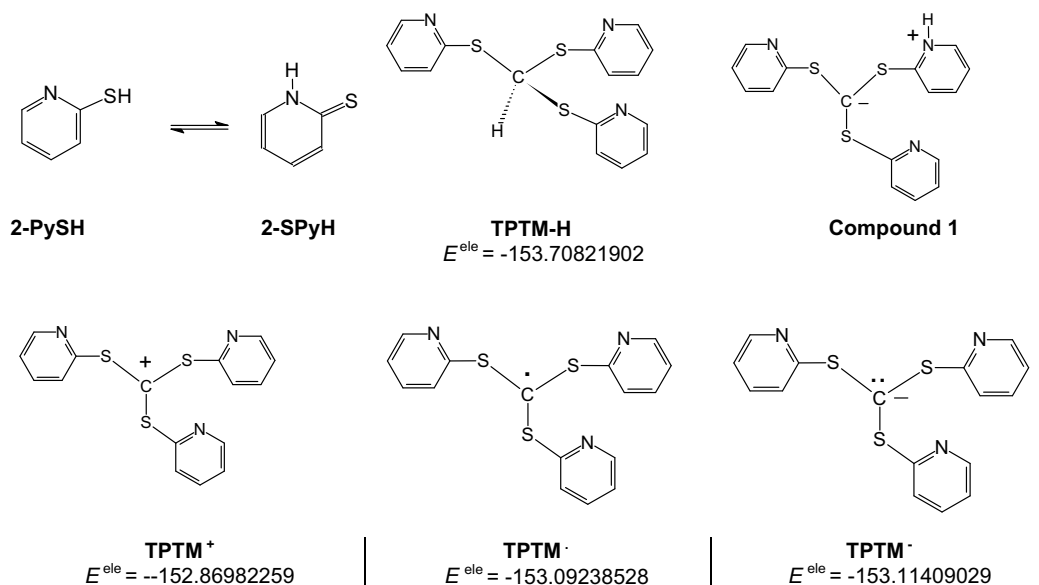


Fig. 1. Compounds indicated in this article. Energy, E^{ele} , in Hartrees, were calculated using CEP-31G optimized geometries.

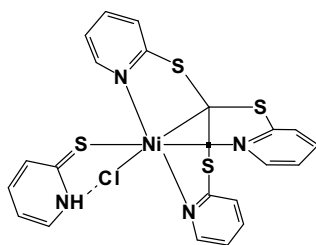


Fig. 2. [Ni(TPTM)(SPyH)Cl].

Electronic spectra were recorded on UV–Vis spectrometer, SHIMADZU – V-2401. Electronic paramagnetic resonance spectra were recorded on a spectrometer consisting of a 500 mW klystron (Varian), a commercial cylindrical resonance cavity (Bruker), an electromagnet (Varian) and a He flux cryosystem (Oxford) for low temperature measurements. Spectra were recorded as first-derivatives using 100 kHz field modulation.

2.2. Synthesis of [Ni(TPTM)(SPyH)Cl]

A saturated solution of NiCl_2 (0.30 g, 2.3 mmol) in water, was added to a solution of TPTM-H [2] (0.80 g, 2.3 mmol) in EtOH (30 ml). The reaction mixture was stirred at room temperature for 3 h and filtered to remove a small amount of a green solid. Crystals of [Ni(TPTM)(SPyH)Cl] formed on slow evaporation of the filtrate, yield: 0.50 g 79%, m.p.: 235–237 °C.

Anal. Calc. for $\text{C}_{21}\text{H}_{16}\text{N}_4\text{S}_4\text{NiCl}$: C, 46.13; H, 2.95; N, 10.25, Ni, 10.74. Found: C, 46.00; H, 3.05; N, 10.26. Ni, 11.05%.

UV–Vis (solid, nm): 450 (sh), 720.

2.3. X-ray structure determination of [Ni{C(Spy)}₃{SPyH}Cl]

Crystals were grown from EtOH solution. The intensity data were collected at 120 K on a Nonius KappaCCD area detector system by the EPSRC X-ray crystallographic service at the University of Southampton, UK. The entire process of data collection, cell refinement and data reduction was accomplished by means of the programs DENZO [8] and COLLECT [9]. Correction for absorption was achieved in each case by a semi-empirical method

based upon the variation of equivalent reflections with the program SADABS [10]. The structures were solved by direct methods in SHELXS-97 [11] within the OSCAIL suite of programs [12] and refined in SHELXL-97 [13]. Approximate positions for H atoms were obtained from difference maps and were refined with a riding model. PLATON was used for the data analysis [14]. The program ORTEP-3 for Windows was used to obtain the figure [15]. Conformational and H-bonding analysis was performed using PLATON [14]. Crystal data and structure refinement details are listed in Table 1.

Table 1
Crystal data and structure refinement for [Ni(TPTM)(SPyH)Cl]

Empirical formula	$\text{C}_{21}\text{H}_{17}\text{Cl}_1\text{N}_4\text{NiS}_4$
Formula weight	547.78
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	
a (Å)	18.8152(5)
b (Å)	9.0624(2)
c (Å)	14.2293(3)
β (°)	111.2940(10)
Volume (Å ³)	2260.61(9)
Z	4
D_{calc} (Mg/m ³)	1.610
Absorption coefficient (mm ⁻¹)	1.364
$F(000)$	1120
Crystal size	0.28 × 0.10 × 0.01 mm
Theta range for data collection	3.07–27.52°
Index ranges	–24 ≤ h ≤ 19; –11 ≤ k ≤ 11; –16 ≤ l ≤ 18
Reflections collected	26512
Independent reflections	5178 [R(int) = 0.0688]
Reflections observed (>2σ)	3931
Data completeness	0.996
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5178/0/280
Goodness-of-fit on F^2	0.903
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0412$ $wR_2 = 0.1167$
R indices (all data)	$R_1 = 0.0664$ $wR_2 = 0.1374$
Largest diffraction peak and hole (e Å ⁻³)	0.776 and –0.817

2.4. Theoretical methodology

The theoretical calculations were carried out using the software package GAUSSIAN03W [16]. Geometry optimization in the gaseous phase was performed using the PM3 semi-empirical method [17]. The spatial arrangements of the PM3 optimized geometries were used as initial models for the HF treatment with the bases sets 6-31G* (HF/6-31G*) and CEP-31G energy minimization calculations in the gaseous phase. The structures obtained from theoretical calculations were characterised as true energy minima on the PES through frequency calculations (when the frequencies are real, a true minimum energy structure is present). The solvent effect (ethanol, $\epsilon = 6.66$) in the geometry optimizations was assessed using the Polarizable Continuum Model (PCM) as implemented in the HF/6-31G* Gaussian 03 package. Calculations (DFT/BLYP/6-31G*) of energy (E_{MO}) and orbital population (c^2) of the occupied and the virtual molecular orbitals (MO's) were made after geometry optimization on the same calculation level. Calculations (DFT/BLYP/6-31G*) of electronic charge (q) were made by the Mulliken method with units in electrons.

3. Results and discussion

3.1. Solid state structure

The complex [Ni(TPTM)(SPyH)Cl] was obtained from the equimolar reaction between TPTM-H and NiCl₂ · 6H₂O in ethanol. As in the reported Cu(II) complexes [5,6], the TPTM⁻ ligand acts as a C,N,N,N-polydentate ligand, arising from deprotonation of the added reagent, TPTM-H, resulting in the formation of three 5-membered chelate rings. Additionally in our case, the added TPTM-H has also partially decomposed to 2(1H)-pyridinethione, SPyH, (and other non-identified fragments): SPyH, a neutral ligand, then bonds to the nickel center via its sulphur atom. The single crystal structure determination at 120(2) K revealed that the Ni(II) cation lies at the centre of a distorted octahedron, see Fig. 3, derived from 3 nitrogen, one carbon, one sulphur and one chlorine donor atoms. The distortion from an ideal octahedral arrangement

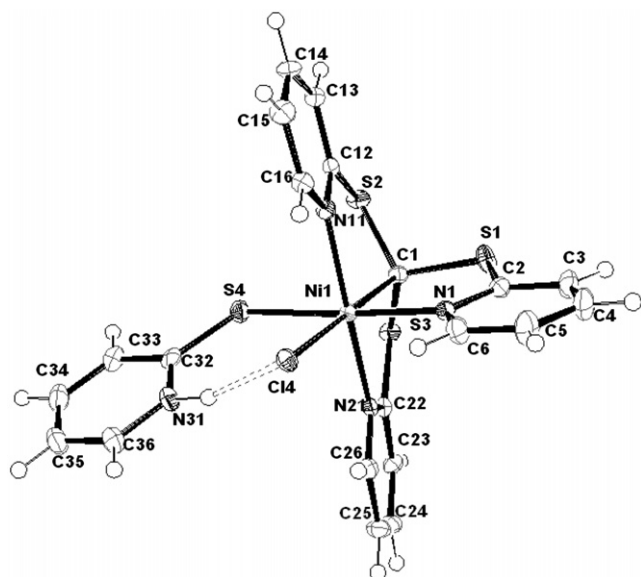


Fig. 3. Atom arrangements and numbering scheme for [Ni(TPTM)(SPyH)Cl]. Probability ellipsoids are drawn at the 50% level; hydrogen atoms are drawn as spheres of arbitrary radius. The intramolecular N31–H31–Cl4 bond is drawn as a dotted line.

Table 2
Selected bond lengths (Å) and angles (°) for [Ni(TPTM)(SPyH)Cl]

Ni(1)–C(1)	2.081(3)	Ni(1)–N(1)	2.121(3)	
Ni(1)–N(21)	2.084(2)	Ni(1)–Cl(4)	2.4128(8)	
Ni(1)–N(11)	2.084(3)	Ni(1)–S(4)	2.6146(9)	
S(1)–C(2)	1.751(3)	S(1)–C(1)	1.813(3)	
S(2)–C(12)	1.763(3)	S(2)–C(1)	1.800(3)	
S(3)–C(22)	1.761(3)	S(3)–C(1)	1.801(3)	
S(4)–C(32)	1.708(3)			
C(32)–C(33)	1.415(5)	C(33)–C(34)	1.374(5)	
C(34)–C(35)	1.413(5)	C(35)–C(36)	1.353(5)	
C(1)–Ni(1)–N(21)	85.18(10)	C(1)–Ni(1)–N(11)	85.26(11)	
C(1)–Ni(1)–N(1)	87.51(11)	Cl(4)–Ni(1)–S(4)	93.48(3)	
N(21)–Ni(1)–N(1)	91.76(10)	N(11)–Ni(1)–N(1)	92.63(10)	
N(21)–Ni(1)–Cl(4)	95.41(7)	N(11)–Ni(1)–Cl(4)	94.24(7)	
N(1)–Ni(1)–Cl(4)	91.42(8)	C(1)–Ni(1)–S(4)	87.58(9)	
N(21)–Ni(1)–S(4)	88.28(7)	N(11)–Ni(1)–S(4)	86.51(7)	
N(1)–Ni(1)–S(4)	175.07(8)	C(1)–Ni(1)–Cl(4)	178.80(9)	
N(21)–Ni(1)–N(11)	169.29(10)			
D–H–A	D–H	H–A	D–A	D–H–A (°)
N(31)–H(31)–Cl(4)	1.03(4)	2.03(4)	3.022(3)	162(3)
C(6)–H(6)–Cl(4)	0.95	2.57	3.234(4)	127
C(16)–H(16)–Cl(4)	0.95	2.75	3.338(3)	121
C(23)–H(23)–Cl(4) ⁱ	0.95	2.82	3.674(4)	151
C(26)–H(26)–Cl(4)	0.95	2.77	3.364(4)	122
C(35)–H(35)–S(4) ⁱⁱ	0.95	2.85	3.599(4)	136

mainly arises from the need to accommodate the four donor atoms of the [TPTM]⁻ ligand around the nickel centre, see Table 2 for selected geometric parameters. The three slightly asymmetrically bonded nitrogen atoms of the [TPTM]⁻ ligand are arranged to form a *mer* configuration with Ni–N bond lengths between 2.0814(3) and 2.121(2) Å: the C atom is in a *cis* position to the Cl⁻ ligand.

There are very few Ni(II) complexes with C,N,N,N-type ligands, and these are generally restricted to carbaporphyrins, confused porphyrins and related compounds, see for example Refs. [18,19]. The [TPTM]⁻ ligand differs from these porphyrin ligands in being a non-cyclic moiety.

The pyridinethione moiety is present in the neutral thione form and is bonded to Ni via S rather than via N or as a chelate. The presence of the pyridinethione form is clear from the variation of the bond lengths within the heterocyclic ring as well as from the C(32)=S(4) bond length, 1.708(3) Å, which is markedly shorter than other C–S bonds present in the molecule – all formally single bond, see Table 2.

The configuration of the complex allows the formation of a strong intramolecular H-bond between the N–H unit of the pyridinethione moiety and the chloride ligand, and three weaker intramolecular C–H–Cl hydrogen bonds, namely C(6)–H(6)–Cl(4), C(16)–H(16)–Cl(4) and C(26)–H(26)–Cl(4) – all of which help to stabilize the molecular structure, see Table 2. As further revealed by the PLATON analysis [14], there are also weak intermolecular C(23)–H(23)–Cl(4)ⁱ and C(35)–H(35)–S(4)ⁱⁱ interactions: symmetry code: (i) $x, -3/2 - y, -1/2 + z$, (ii) $-x, -1/2 + y, 1/2 - z$, which combine to link the molecules into a 3D array. Each type of intermolecular interactions is shown separately in Fig. 4a and b. Fig. 4a illustrates both the intramolecular and chain-forming intermolecular C–H–Cl interactions, while Fig. 4b shows the C(35)–H(35)–S(4)ⁱⁱ interactions. Interestingly, both the hydrogen bonding acceptor and donor atoms in the chain forming C(35)–H(35)–S(4) interactions are found in the pyridinethione ligand.

3.2. EPR study

The EPR spectra of a powdered sample of [Ni(TPTM)(SPyH)Cl] and that of NiCl₂ · 6H₂O, both measured at 25 K in X-band (9.3877 GHz), are shown in Fig. 5. The spectrum of [Ni(TPTM)(SPyH)Cl] exhibits a very broad signal associated to Ni²⁺ with a

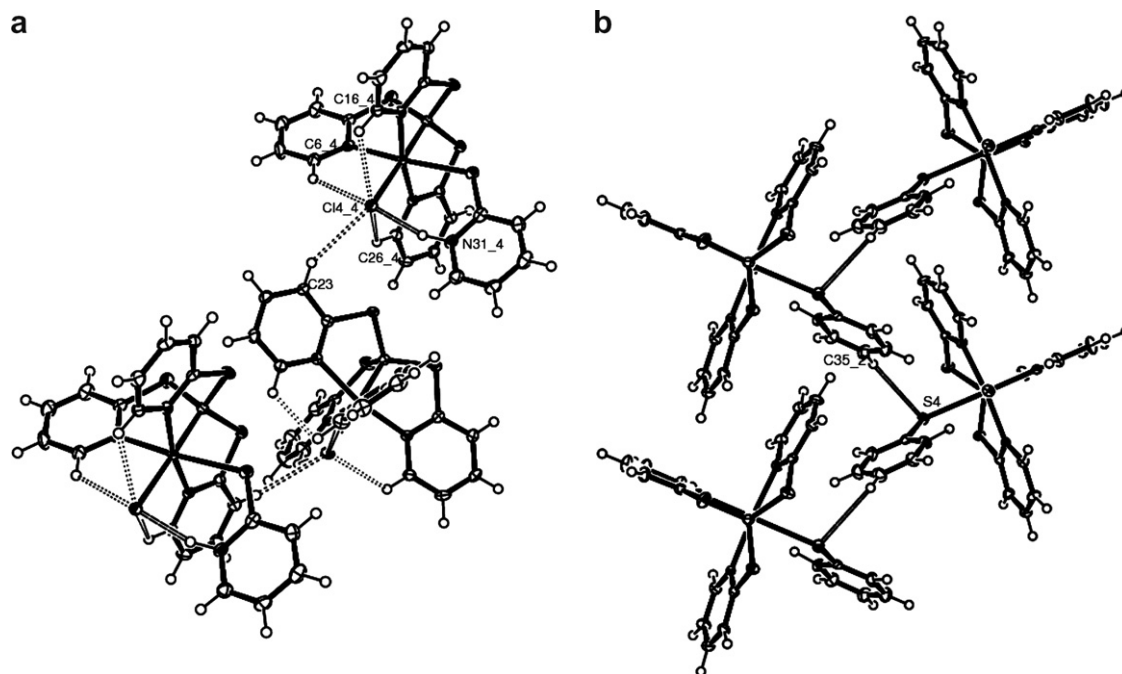


Fig. 4. Hydrogen-bonding in $[\text{Ni}(\text{TPTM})(\text{SPyH})\text{Cl}]$. (a) Intramolecular and chain-forming intermolecular C–H–Cl hydrogen bonding, shown in dashed lines; (b) intermolecular C(35)–H(35)–S(4) hydrogen bonds forming chains, shown in double dotted lines.

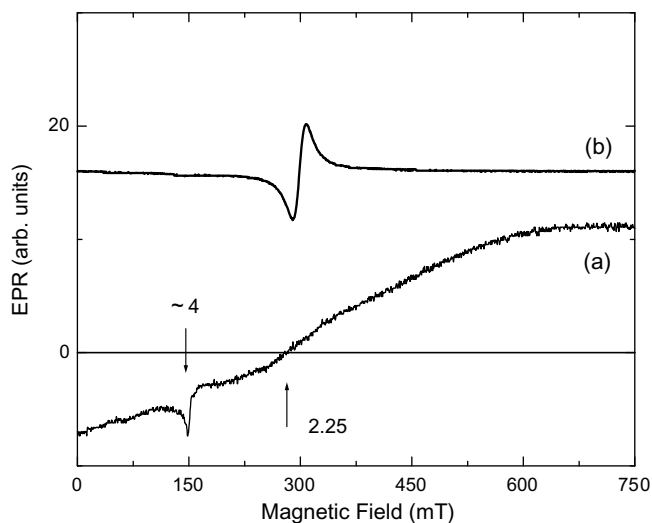


Fig. 5. X Band ESR spectra measured at 20 K for (a) $[\text{Ni}(\text{TPTM})(\text{SPyH})\text{Cl}]$ and (b) $\text{NiCl}_2 \cdot 6(\text{H}_2\text{O})$ X band EPR spectra measured at 20 K; arrows indicate g factors.

g -factor of about 2.25(5) which is typical for the Ni^{2+} ion ($3d^8$) with $S = 1$. In this case, the electronic fine structure is large compared to the electron Zeeman interaction leading to a single line. The g factor deviates strongly from 2 because of strong spin-orbit coupling. In the figure xx the feature at about 150 mT ($g \sim 4.3$) is associated to a little Ni^{3+} impurity (equivalent to Co^{2+} with $3d^7$ and $S = 3/2$). Although the shortest Ni–Ni distance was determined to be very long (8.56 Å) along the b axis, magnetic exchange coupling cannot be neglected for explaining the large line width [20]. In addition, Ni^{2+} ions are very sensitive to small local distortions and fine structure anisotropy. Because of the broad line width no other structural details can be obtained from the EPR measurements. Attempts to grow suitably large crystals for single crystal EPR spectra are continuing.

3.3. Theoretical studies

An optimized geometry study of the complex did not reveal significant Ni–SPyH contacts in the gas phase as shown by the Ni–S calculated bond length of 5.763 Å. This is stark contrast to the observation of the relatively strong Ni–S bond [2.6145(9) Å] in the solid state as shown by the X-ray crystallographic study. Dissociation of the complex, i.e. loss of the 2-PySH ligand, is also a possibility in solution.

3.4. Deprotonation of TPTM-H

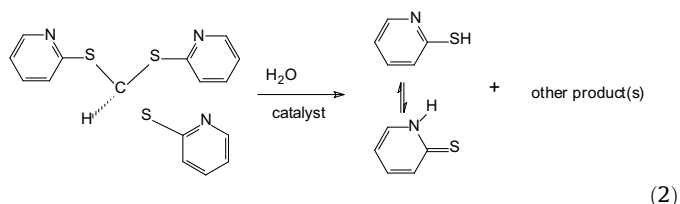
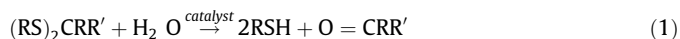
The deprotonation of TPTM-H leading to the formation of $[\text{Ni}(\text{TPTM})(\text{PySH})\text{Cl}]$ was of interest to us. The hydrogen atom in TPTM-H is acidic due to the adjacent polarisable sulphur atoms. While the $\text{p}K_a$ of TPTM-H is unknown, those of other $(\text{RS})_3\text{CH}$ compounds confirm the acidic natures of such hydrogens, e.g., the $\text{p}K_a$ determined for $(\text{PhS})_3\text{CH}$ in Me_2SO was 22.8 [21a] and ready metallation of $(\text{PhS})_3\text{CH}$ occurs on reaction with organolithium reagents to give $(\text{PhS})_3\text{CLi}$ [21b].

Our earlier X-ray crystallography study indicated a short N–H contact of 2.534(8) Å in solid TPTM-H [2]: the very broad CH signal observed in the ^1H NMR spectrum suggests that this N–H interaction persists in solution [2]. DFT/BLYP/6-31G* calculations indicated that all three nitrogens are interacting intramolecularly with the C–H atom in the gas phase. Such N–H interactions, and consequently weakening of the C–H bond, will clearly facilitate deprotonation. Furthermore, the formation of the C,N,N,N chelated system must be a positive factor in the deprotonation of TPTM-H. Overall, metallation of TPTM-H does not appear too surprising even with NiCl_2 .

Theoretical calculations were carried out at the CEP-31G level on the optimized geometries and energies of TPTM-H, its cation, free radical and carbanion, TPTM⁺, TPTM[•], and TPTM[−], see Fig. 1. As expected, the calculations indicated that TPTM[−] is the most stable transient, suggesting that deprotonation of TPTM-H is more probable *via* transfer of H^+ , rather than as H^{\bullet} or H^- .

3.5. Formation of 2-(1H)-pyridinethione

The formation of 2H-pyridinethione in the reaction between NiCl₂ and TPTM-H in aqueous EtOH is also of interest since, in previous reports of the copper [5,6] and organotin reactions [7], there were no mentions of TPTM-H decomposition products. Furthermore, we have recently isolated Bi(SPy)₃ in high yield from the reaction of Bi(NO₃)₃ with TPTM-H in aqueous EtOH: no Bi complex with [TPTM] has been isolated [22]. Our samples of TPTM-H were found to be completely free of its precursor, 2H-pyridinethione, and hence the 2H-pyridinethione (or 2-pyridinethiol) had to be generated during the reactions. What other product was formed remains unknown. The formation of 2H-pyridinethione can be considered as a dethioketalization/dethioacetalization reaction of TPTM-H: Eq. (1) indicates the general reaction, while Eq. (2) illustrates the specific findings in this study.



There is a vast literature on the protection of carbonyl compounds as thioacetal and thioketal derivatives [23,24]. Removal of the protecting groups to give back the carbonyl compound has also well been reported, with a variety of conditions being used [24], including the use of different acid and metal salt catalysts. Among the metal salts reported to catalyze dethioketalization reactions are copper salts [25], mercury salts [26], iron salts [27] and bismuth salts [28,29]. The formation of thioacetals and thioketals from their components and the removal of the thiols to give back carbonyl compounds are reversible reactions; for example, metal salts, such as bismuth triflate [28] and nitrate [24], are able to catalyze the formation of thioacetals and thioketals as well as their decomposition. Formation and dethioketalization of the thioacetals/thioketals clearly depends on the relative concentrations of reagents and removal of selected products.

DFT/BLYP/6-31G* calculations were also carried out on an intramolecular proton transfer from TPTM-H to give [(2-PyS)⁻-S-C5H4NH⁺] (**1**), [Fig. 1] as an initial step in the formation of 2H-pyridinethione. Species **1** was found to be more energetic than TPTM-H by only 25.27 kcal and so a pathway *via* **1** is a possibility.

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Appendix A. Supplementary material

CCDC 676186 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.02.031](https://doi.org/10.1016/j.jorganchem.2008.02.031).

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