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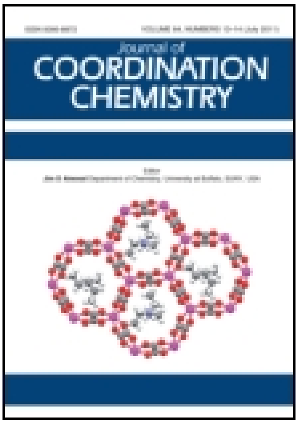

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Synthesis, characterization, and structures of nickel(II) and palladium(II) complexes of aromatic thiohydrazides

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Nickel(II) and palladium(II) form neutral 1 : 2 chelates with aromatic thiohydrazides, for example. thiobenzhydrazide, *o*-hydroxythiobenzhydrazide, furan-2-thiohydrazide, and thiophen-2-thiohydrazide. All the compounds are diamagnetic and have been characterized by elemental analysis and spectroscopic methods. *o*-Hydroxythiobenzhydrazido complexes of nickel(II) and palladium(II) were crystallized from DMSO and their structures were solved by X-ray diffraction. The complexes are isostructural with planar structures. Metal ion is linked to two identical deprotonated ligands through *trans* hydrazinic nitrogen and sulfur. Hydrogen of OH is involved in intramolecular hydrogen-bonding.

Keywords: Nickel(II); Palladium(II); Thiohydrazides; Spectroscopy; X-ray crystallography

1. Introduction

Thiosemicarbazides and thiosemicarbazones are an important class of nitrogen–sulfur donors because of their interesting chemical [1–4], analytical [5, 6], and biological properties [7]. The important biological properties include antibacterial [8], antifungal [9], antitumor [10], and antiviral activity against influenza [11] and small pox [12] viruses. In several cases the pharmacological activity of these compounds has been enhanced by coordinated metal ions [13, 14]. Isonicotinic acid hydrazide is a drug for treatment of tuberculosis [15] and its activity has been correlated with its chelate forming ability [16]. Recently, a model compound of the active site of nickel superoxide dismutase has been shown to have N_2S_2 donors [17]. A palladium complex of thiobenzoylhydrazone is a chemoselective homogeneous hydrogenation catalyst of phenylacetylene to styrene [18]. Thiohydrazides are closely related to thiosemicarbazides and may be represented as $RCSNHNH_2$ (where R = an alky, an aryl, or a heterocyclic group). They are simpler than thiosemicarbazides in the sense that N^4 NH_2 group is absent in these ligands, but the presence of $-CSNHNH_2$ would make thiohydrazides excellent N–S chelates just like thiosemicarbazides. Their transition metal complexes should also possess diverse biological properties similar to those of

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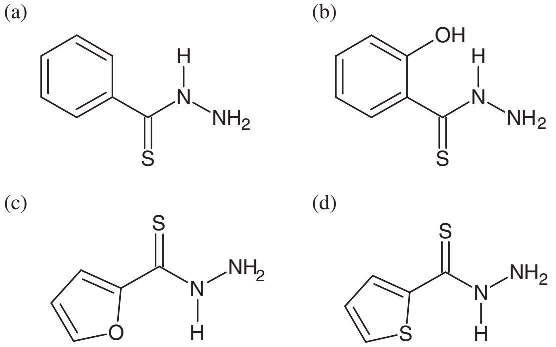

Figure 1. Structural formulae of the ligands used for the synthesis of nickel(II) and palladium(II) complexes: (a) thiobenzhydrazide (Htbh), (b) *o*-hydroxythiobenzhydrazide (Hhtbh), (c) furan-2-thiohydrazide (Hfth), and (d) thiophene-2-thiohydrazide (Htth).

thiosemicarbazides and thiosemicarbazones. In the present communication, synthesis and characterization of nickel(II) and palladium(II) complexes of four aromatic thiohydrazide ligands are described. Structural formulae of the ligands are shown in figure 1. Structures of $Ni(htbh)_2 \cdot 2(CH_3)_2SO$ and $Pd(htbh)_2 \cdot 2(CH_3)_2SO$ have been established by X-ray crystallography.

2. Experimental

2.1. *Materials and methods*

$NiCl_2 \cdot 2H_2O$ (G.R, E. Merck, Germany), $Ni(NO_3)_2 \cdot 6H_2O$ (G.R, E. Merck, Germany), and $PdCl_2 \cdot 2H_2O$ (J.M., UK) were used to prepare stock solution of the corresponding metal. All other chemicals were of reagent grade and used without further purification; solvents were purified and dried according to standard procedures. Electronic absorption, IR, and proton NMR spectra were recorded on a Hitachi-U-3210 spectrophotometer, Unicam 300S (KBr discs, $4000-300\,cm^{-1}$) and Bruker 500 MHz instruments, respectively. Conductivity of $10^{-3}\,molL^{-1}$ solution of the compounds in freshly distilled DMSO was measured with a Systronics (India) Model 304 conductivity bridge. Microanalyses and magnetic moment measurements were carried out at the Indian Association for the Cultivation of Sciences, Jadavpur, Kolkata. Ligands were prepared as described earlier [19].

2.2. *Preparation of bis-thiohydrazido complexes of nickel(II)*

An aqueous solution of $NiCl_2$ containing 0.2 mmol of the metal was diluted to about 100 mL, heated to 80°C, and an ethanolic solution containing 0.6 mmol of the ligand was added. The pH of the solution was adjusted between 5.6 and 6.8 with 10% sodium acetate solution. Yellowish green precipitate formed was digested on a boiling water bath for 1 h and filtered through a sintered glass crucible. The residue was washed thoroughly with hot water and dried at 110°C. The yield was >99.5% in each case on the basis of nickel(II).

[Ni(tbh)$_2$]: Anal. Calcd for [Ni($C_7H_7N_2S$)$_2$]: C, 46.58; H, 3.88; N, 15.53; S, 17.74; Ni, 16.27. Found (%): C, 46.42; H, 3.97; N, 15.31; S, 17.86; Ni, 16.27.

[Ni(htbh)$_2$]: Anal. Calcd for [Ni($C_7H_7N_2OS$)$_2$]: C, 42.93; H, 3.48; N, 14.32; S, 16.30; Ni, 14.88. Found (%): C, 43.78; H, 3.57; N, 14.26; S, 16.22; Ni, 14.85.

[Ni(fth)$_2$]: Anal. Calcd for [Ni($C_5H_5N_2OS$)$_2$]: C, 35.22; H, 2.94; N, 16.51; S, 18.79; Ni, 17.23. Found (%): C, 35.00; H, 2.89; N, 16.51; S, 18.87; Ni, 17.01.

[Ni(tth)$_2$]: Anal. Calcd for [Ni($C_5H_5N_2S_2$)$_2$]: C, 32.20; H, 2.68; N, 15.14; S, 34.34; Ni, 15.63. Found (%): C, 32.32; H, 2.54; N, 15.14; S, 34.50 Ni, 15.66.

2.2.1. Crystallization of [Ni(htbh)$_2$]. The complex was dissolved in freshly distilled DMSO to prepare a saturated solution and allowed to stand for 24 h. Brown crystals of [Ni(htbh)$_2$] · 2DMSO were separated by filtration, washed with DMSO–water (1 : 5) mixture and dried in vacuum.

[Ni(htbh)$_2$] · 2DMSO: Anal. Calcd. for $C_{18}H_{26}N_4NiO_4S_4$: C, 39.37; H, 4.74; N, 10.21; S, 23.33; Ni, 10.70. Found (%): C, 39.59; H, 4.23; N, 10.30; S, 23.17; Ni, 10.65.

2.3. *Preparation of bis-thiohydrazido complexes of palladium(II)*

An aqueous solution of $PdCl_2$ containing 0.2 mmol of the metal was diluted to about 100 mL and heated nearly to boiling. To the hot solution an ethanolic solution of the ligand (0.8 mmol) was added and pH of the solution was adjusted between 5.4 and 6.0 with 10% sodium acetate solution. It was digested on a boiling water bath for 1 h. The light yellow precipitate was collected by filtration through a sintered glass crucible, washed with hot water and dried at 120°C. The yield in each case was almost quantitative on the basis of palladium(II).

[Pd(tbh)$_2$]: Anal. Calcd for [Pd($C_7H_7N_2S$)$_2$]: C, 41.13; H, 3.43; N, 13.71; S, 15.67; Pd, 26.06. Found (%): C, 41.00; H, 3.52; N, 13.83; S, 15.55; Pd, 25.99.

[Pd(htbh)$_2$]: Anal. Calcd for [Pd($C_7H_7N_2OS$)$_2$]: C, 38.15; H, 3.18; N, 12.72; S, 14.53; Pd, 24.16. Found (%): C, 38.34; H, 3.02; N, 12.91; S, 14.50; Pd, 24.07.

[Pd(fth)$_2$]: Anal. Calcd for [Pd($C_5H_5N_2OS$)$_2$]: C, 30.89; H, 2.57; N, 14.42; S, 16.48; Pd, 27.40. Found (%): C, 30.95; H, 2.60; N, 14.35; S, 16.37; Pd, 27.50.

[Pd(tth)$_2$]: Anal. Calcd for [Pd($C_5H_5N_2S_2$)$_2$]: C, 28.54; H, 2.38; N, 13.32; S, 30.22; Pd, 25.31. Found (%): C, 28.62; H, 2.29; N, 13.41; S, 30.25 Pd, 25.26.

2.3.1. Crystallization of [Pd(htbh)$_2$]. A saturated solution of the complex was prepared by dissolving it in freshly distilled DMSO and allowing to stand for 24 h. Yellow crystals of [Pd(htbh)$_2$] · 2DMSO were separated by filtration, washed with DMSO–water (1 : 5) mixture and dried in vacuum.

[Pd(htbh)$_2$] · 2DMSO: Anal. Calcd for $C_{18}H_{26}N_4PdO_4S_4$: C, 36.22; H, 4.36; N, 9.39; S, 21.46; Pd, 17.84. Found (%): C, 36.11; H, 4.23; N, 9.58; S, 21.58; Pd, 17.9.

2.4. *X-ray crystallography*

X-ray diffraction data were collected at 293(3) K using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Nonious DIP – 1030 H single crystal diffractometer. Cell refinements, indexing, and scaling of the data sets were performed using Denzo and Scalepack [20]. The contribution of hydrogen atoms at calculated positions was included in final cycles of refinement. The structures were solved by Patterson and subsequent Fourier analyses [21] and refined by full-matrix least-squares based on F^2 with all observed reflections using SHELX97 [21]. All calculations were performed using the WinGX System, Ver 1.70.01 [22].

3. Results and discussion

3.1. *Electronic spectra*

Absorption maxima in electronic spectra of thiohydrazide complexes of nickel(II) and palladium(II) in ethanol and DMSO with their assignments are available as Supplementary material. All the nickel(II) and palladium(II) complexes of thiohydrazide derivatives were considered to have planar, distorted D_{2h} symmetry and assignments were made on the basis of electronic spectra of bis(maleonitrile dithiolato) complexes of nickel(II) and palladium(II) reported earlier [23, 24].

The thiohydrazide complexes of nickel(II) showed 6–8 maxima from 210 to 800 nm. At least four bands are very intense [$\varepsilon > 1000\,(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$] and may be assigned as metal–to-ligand [M → L] or ligand-to-metal [L → M] charge transfer (MLCT or LMCT) transition or ligand centered [L → L] bands. The weak bands that have molar extinction coefficient less than 300 $(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$ are assigned as Laporte forbidden d–d transitions. The abnormal high intensity of the d–d transition bands may be ascribed to the asymmetric nature of the ligands or the bands may have stolen intensity from the charge transfer bands.

The most interesting observation in electronic spectra of nickel(II) thiohydrazide complexes is the presence of bands at 760–780 nm. Considering their molar extinction coefficients and solvatochromatism such bands are assigned as MLCT. The bands are unsymmetrical and broadened toward the lower wavelength side, so the band is probably an envelope of two closely spaced MLCT bands, $d_{x^2-y^2} \rightarrow L(\pi)^*$, $^1A_g \rightarrow {}^1A_{2u}^*$ and $^1A_g \rightarrow {}^1B_{2u}^*$.

The palladium(II) complexes, however, lack any such high-intensity charge transfer bands in the long wavelength region, in agreement with the spectra of palladium(II) complexes reported earlier [23, 24].

Broad bands with very low intensities ($\varepsilon < 300\,(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$) situated in the 440–680 nm region are assigned as parity forbidden d–d transition. On going from nickel(II) to palladium(II) d–d bands shift progressively to shorter wavelength, i.e. higher energy (from 14,700 $\mathrm{cm^{-1}}$ to 22,570 $\mathrm{cm^{-1}}$). Some d–d transitions have been obscured by high-intensity charge transfer bands in the shorter wavelength region.

Nickel(II) complexes in ethanol exhibit a high-intensity sharp charge transfer band at 350–390 nm and another at 260–270 nm with an energy difference of nearly 10,500–11,000 $\mathrm{cm^{-1}}$ and are assigned to allowed $L(\pi) \rightarrow M(xy)$ and $L(\sigma) \rightarrow M(xy)$ charge transfer bands, respectively. The band at 260–270 nm could not be observed in DMSO because of strong absorption of solvent in that region. Such bands are also common for palladium(II) complexes as well, with energy difference of 11,500–120,00 cm^{-1}.

In the shorter wavelength region, another set of high-intensity bands are almost unaffected by change of solvent polarity and are assigned as $\text{L} \rightarrow \text{L}$ transitions. The lowest energy band corresponds to $n \rightarrow \pi^*(g \rightarrow g)$ followed by $\pi \rightarrow \pi^*(u \rightarrow g)$ and $n \rightarrow \sigma^*(g \rightarrow u)$ transitions. On comparison of spectra of Hhtbh and Htth in ethanol and that of corresponding complexes, the band at 300–320 nm may be assigned as $\text{L} \rightarrow \text{L}$ band of lowest energy. Other ligand centered transitions are probably obscured by high-intensity LMCT bands in some cases.

3.2. *IR spectra*

Significant bands in IR spectra of the substituted thiohydrazides and the corresponding nickel(II) and palladium(II) complexes are available as Supplementary material. Broad bands near 3300–3200 cm^{-1} are assigned as N–H stretching frequency [25, 26]. These bands shift to higher frequency in the corresponding metal complexes. The number of bands in the complexes is greater than those in the free ligands. The spectral pattern is similar to that observed in *trans*-bis (glycinato) platinum(II) [27] and *trans*-bis (thiosemicarbazide) nickel(II) sulfate, trihydrate [28]. The *cis* complexes show broad bands due to N–H stretch but *trans* complexes show a sharp band. The region near 450 cm^{-1} also shows features of *trans*-complex formation by two distinct peaks at ~435 and ~330 cm^{-1}. Thus the prepared substituted thiohydrazide complexes of nickel(II) and palladium(II) are *trans*. The bending mode of vibration for $-\text{NH}_2$ (β_{NH_2}) is observed near 1600 cm^{-1} [29] in free ligands and shift to higher frequency in the complexes, indicating complexation through hydrazinic $-\text{NH}_2$. The $\nu_{\text{C–N}}$ band [Amide II] is observed at 1580–1500 cm^{-1} [30] for the ligands and shift to higher frequency in corresponding complexes.

Bands for $\nu_{\text{C–S}}$ are very difficult to assign [31] as the position and intensity of bands other than pure C–S stretches suffer a change due to coordination through sulfur. Coupled vibration gives $\nu_{\text{C–S}}$ near $\nu_{\text{C–N}}$, aromatic $\nu_{\text{C–C}}$, and δ_{NH_2} modes. In thioformamide, the band with most C–S character was assigned at 843 cm^{-1} [32]. A band at 699 cm^{-1} has also been assigned as $\nu_{\text{C–S}}$ for thioamide [32]. In thiosemicarbazide, $\nu_{\text{C–S}}$ has been assigned [33] at 803 cm^{-1} and is reported to have more than 50% contribution of C–S stretch. Intensity ratio $\nu_{\text{C=O}}/\nu_{\text{C=S}}$ of 1.38–1.5 enables the assignment [32] of $\nu_{\text{C–S}}$ in substituted thiohydrazide and their corresponding nickel(II) and palladium(II) complexes. The $\nu_{\text{C–S}}$ in the ligands undergoes a shift to lower frequency in the complexes, indicating thioenolization before complex formation. A very weak band was observed at ~2560 cm^{-1}, assigned to $\nu_{\text{S–H}}$ [34]. The band may arise from thioenolization of the ligand and its weakness is probably due to shift of the equilibrium to the left of the following tautomerization:

$$-\text{C}(=\text{S})-\text{NH}-\text{NH}_2 \leftrightarrow \text{C}-(\text{S}-\text{H}) = \text{N}-\text{NH}.$$

The absence of $\nu_{\text{S–H}}$ in the complexes indicates coordination through sulfur and thioenolization takes place prior to complex formation [34].

The metal–nitrogen stretching frequency was observed at 550–530 cm^{-1} [35] and the band at 450–385 cm^{-1} may be assigned as $\nu_{\text{M–S}}$ [35, 36]. Both bands are absent in free ligands.

3.3. *^{1}H NMR spectra*

Chemical shift data for ^{1}H NMR spectra of the substituted thiohydrazides and their corresponding nickel(II) and palladium(II) complexes are available as Supplementary material. NMR spectra of Hhtbh have four signals at $\delta = 6.67$, 6.84, 7.08, and 7.1 attributed to the four protons attached to benzene. These peaks undergo a negligible shift on complex formation. The amidic proton resonance at $\delta = 10.4$–12 ppm (1H) in ligands are absent in the complexes, suggesting involvement of deprotonated ligands in complex formation. The NMR signals of hydrazinic proton (2H) in the ligand ($\delta = 5.1$–6.1 ppm) underwent downfield shifts by more than 1 ppm, indicating coordination through hydrazinic nitrogen [9, 37].

3.4. *X-ray crystallography*

Crystal data, together with the details of data collection and structure refinement parameters, are summarized in table 1. Selected bond lengths and angles are presented in table 2. ORTEP diagrams along with numbering schemes of $[Ni(C_7H_7N_2OS)_2] \cdot 2(CH_3)_2SO$ and $[Pd(C_7H_7N_2OS)_2] \cdot 2(CH_3)_2SO$ are shown in figures 2 and 3, respectively.

X-ray crystallography shows that $[Ni(C_7H_7N_2OS)_2] \cdot 2(CH_3)_2SO$ contains discrete $[Ni(C_7H_7N_2OS)_2]$ entities and two DMSO molecules. The nickel(II) ions are four

Table 1. Crystal data and refinement details of $[Ni(htbh)_2] \cdot 2(CH_3)_2SO$ and $[Pd(htbh)_2] \cdot 2(CH_3)_2SO$.

	$[Ni(htbh)_2] \cdot 2(CH_3)_2SO$	$[Pd(htbh)_2] \cdot 2(CH_3)_2SO$
Empirical formula	$C_{18}H_{26}N_4NiO_4S_4$	$C_{18}H_{26}N_4PdO_4S_4$
Formula weight	549.38	597.07
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	13.417(4)	13.462(4)
b	7.988(3)	8.002
c	12.413(3)	12.478(3)
α	90	90
β	112.18(3)	111.44(3)
γ	90	90
Volume (Å^3), Z	1231.9(7), 2	1251.2(7), 2
Calculated density (Mg m^{-3})	1.481	1.585
Absorption coefficient (mm^{-1})	1.158	1.585
$F(000)$	572	608
θ range for data collection (°)	3.11–29.61	3.18–30.07
Reflections collected/unique	14,810/3162 [R(int) = 0.0502]	14,622/3467 [R(int) = 0.0449]
Crystal size (mm^3)	Not determined	$0.45 \times 0.20 \times 0.12$
Completeness to θ (%)	91.4	98.2
Max. and min. transmission	0.8085 and 0.5632	0.8704 and 0.5668
Data [$I > 2\sigma(I)$]/parameters	2019/147	2479/147
Goodness-of-fit on F^2	0.894	0.888
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0365$, $wR_2 = 0.0935$	$R_1 = 0.0340$, $wR_2 = 0.0819$
R indices (all data)	$R_1 = 0.0591$, $wR_2 = 0.0993$	$R_1 = 0.0471$, $wR_2 = 0.0858$
Largest difference peak and hole (e Å^{-3})	0.245 and −0.293	0.483 and −0.303

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

$\mathrm{GOF} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{½}$.

Table 2. Selected bond lengths (Å) and angles (°) in the metal coordination sphere.

$[Ni(htbh)_2]\cdot 2(CH_3)_2SO$		$[Pd(htbh)_2]\cdot 2(CH_3)_2SO$	
Ni–N(1)	1.8913(17)	Pd–N(1)	2.028(2)
Ni–N(1′)	1.8913(17)	Pd–N(1′)	2.028(2)
Ni–S(1′)	2.1640(8)	Pd–S(1′)	2.2834(9)
Ni–S(1)	2.1640(8)	Pd–S(1)	2.2834(9)
S(1)–C(7)	1.733(2)	S(1)–C(7)	1.738(2)
O(1)–C(1)	1.359(3)	O(1)–C(1)	1.358(3)
N(1)–N(2)	1.455(2)	N(1)–N(2)	1.447(3)
N(2)–C(7)	1.297(2)	N(2)–C(7)	1.291(3)
S(2)–O(2)	1.5130(18)	S(2)–O(2)	1.5160(19)
S(2)–C(8)	1.776(3)	S(2)–C(8)	1.771(4)
S(2)–C(9)	1.782(3)	S(2)–C(9)	1.782(3)
N(1)–Ni–N(1′)	180.0	N(1)–Pd–N(1′)	180.0
N(1)–Ni–S(1′)	92.17(6)	N(1)–Pd–S(1′)	84.69(6)
N(1′)–Ni–S(1′)	87.83(6)	N(1′)–Pd–S(1′)	95.31(6)
N(1)–Ni–S(1)	87.83(6)	N(1)–Pd–S(1)	95.31(6)
N(1′)–Ni–S(1)	92.17(6)	N(1′)–Pd–S(1)	84.69(6)
S(1′)–Ni–S(1)	180.00(3)	S(1′)–Pd–S(1)	180.00(3)
C(7)–S(1)–Ni	96.74(8)	C(7)–S(1)–Pd	96.77(8)
N(2)–N(1)–Ni	119.05(13)	N(2)–N(1)–Pd	118.16(14)
C(7)–N(2)–N(1)	113.48(17)	C(7)–N(2)–N(1)	115.7(2)
O(1)–C(1)–C(6)	116.7(2)	O(1)–C(1)–C(6)	117.3(2)
O(1)–C(1)–C(2)	122.9(2)	O(1)–C(1)–C(2)	122.5(2)
C(6)–C(1)–C(2)	120.4(2)	C(6)–C(1)–C(2)	120.2(2)
N(2)–C(7)–C(2)	116.55(18)	N(2)–C(7)–C(2)	116.2(2)
N(2)–C(7)–S(1)	122.87(16)	N(2)–C(7)–S(1)	124.67(18)
C(2)–C(7)–S(1)	120.57(15)	C(2)–C(7)–S(1)	119.08(17)
O(2)–S(2)–C(8)	105.95(13)	O(2)–S(2)–C(8)	105.68(15)
O(2)–S(2)–C(9)	105.76(12)	O(2)–S(2)–C(9)	105.61(14)
C(8)–S(2)–C(9)	98.69(17)	C(8)–S(2)–C(9)	98.83(19)

Symmetry transformations used to generate equivalent atoms: 1′: $-x$, $-y+1$, $-z+1$.

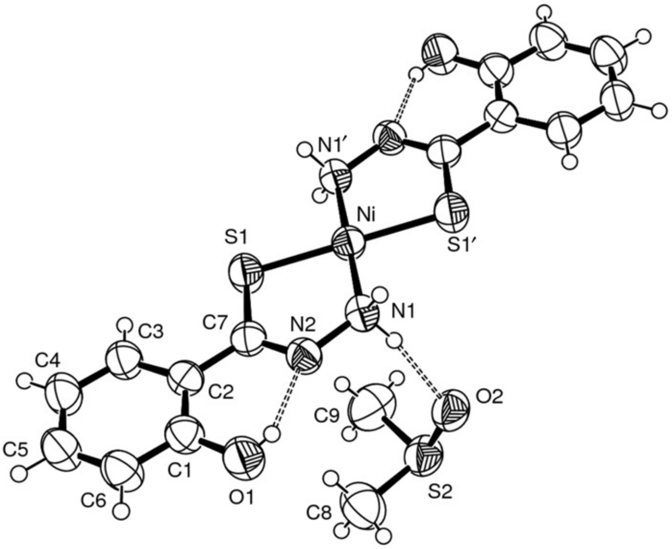

Figure 2. ORTEP diagram (50% probability) of the structure of $[Ni(htbh)_2]\cdot 2DMSO$ showing atom-numbering scheme. One DMSO attached to N1′ has not been shown in the figure.

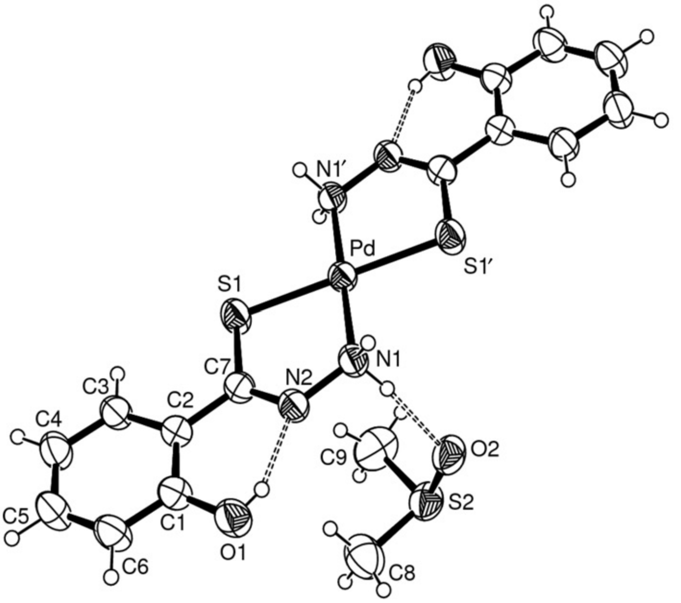

Figure 3. ORTEP diagram (50% probability) of $[Pd(htbh)_2] \cdot 2DMSO$ showing atom-numbering scheme. One DMSO attached to N1′ has not been shown in the figure.

coordinate with two nitrogen atoms and two sulfur atoms from two identical bidentate ligands forming a planar structure with *trans* configuration. $[Pd(C_7H_7N_2OS)_2] \cdot 2(CH_3)_2SO$ is isostructural with the corresponding nickel complex. The M–N and M–S (M = Ni or Pd) bond lengths are 1.8913(17) and 2.1640(8) Å for the nickel complex whereas those for palladium complex are 2.028(2) and 2.2834(9) Å, respectively, falling within the normal range of M–N and M–S bond lengths of nickel(II) and palladium(II) complexes of thiosemicarbazide and thiosemicarbazone [38, 39]. The C(7)–S(1) bond lengths of the crystals of the nickel(II) and palladium(II) complexes are 1.733(2) and 1.738(2) Å, respectively, larger than C=S bond length of 1.61–1.63 Å [40]. Similarly C(7)–N(2) bond lengths of 1.297(2) and 1.291 Å are shorter than C–N single bond length of 1.47 Å. From these data it is obvious that thioenol tautomer of the ligand participates in complex formation [41].

There is an extensive set of hydrogen bonds (table 3) with O(1)H and O(1′)H involved in intramolecular hydrogen-bonding with N(2) and N(2′), respectively, with identical $O \cdots N$ distance of 2.552 Å in the nickel complex and 2.549 Å in the palladium complex. O(1) also establishes simultaneously two short contacts (less than the sum of van der Waals radii) with C(9)H(9)\$1 and C(3)H(3)\$1 with $C(9)\$1 \cdots O(1)$ and $C(3)\$1 \cdots O(1)$ distances of 3.433 Å and 3.374 Å in the nickel complex and 3.432 Å and 3.375 Å in the palladium complex. These hydrogen bonds along with short contacts play a vital role in crystal formation [38] and may be the reason why complexes of other ligands like Htbh, Hfth, or Htth could not be crystallized. The complex crystallizes with two molecules of DMSO as solvent of crystallization. Oxygen of each DMSO forms

Table 3. Hydrogen bond lengths (Å) and angles (°).

		$Ni(C_7H_7N_2OS)_2 \cdot 2(CH_3)_2SO$			$Pd(C_7H_7N_2OS)_2 \cdot 2(CH_3)_2SO$		
Donor (D)	Acceptor (A)	H···A	D–H···A	D···A	H···A	D–H···A	D···A
O(1)–H(1)	N(2)	1.938	145.51	2.552	1.864	159.79	2.549
N(1)–H(1A)	O(2)	1.991	170.20	2.882	1.964	172.02	2.858
N(1)–H(1B)	O(2)$1	1.997	168.00	2.883	1.967	172.98	2.862
C(9)–H(9B)$1	O(1)	2.636	140.58	3.433	2.606	144.47	3.432
C(3)–H(3)$1	O(1)	2.543	144.87	3.374	2.559	146.74	3.375

$1: Represents atoms from other molecule of $M(C_7H_7N_2OS)_2 \cdot 2(CH_3)_2SO$.

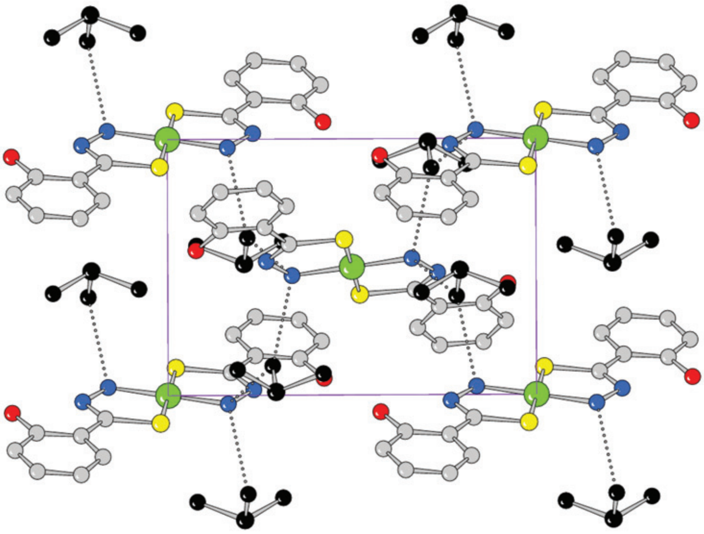

Figure 4. 2-D layered structure through NH···O(DMSO) H-bond connections (DMSO in black).

bifurcated hydrogen bonds with two different hydrazinic $–NH_2$ groups. Hydrogen-bonding between oxygen of DMSO and hydrogen of hydrazinic nitrogen leads to the formation of a layered structure as shown in figure 4.

4. Conclusion

This study reveals that nickel(II) and palladium(II) form stable, diamagnetic, innermetallic 1 : 2 *trans* complexes with thiohydrazide ligands binding through hydrazinic nitrogen and sulfur. From the crystal structures of $Ni(htbh)_2 \cdot 2(CH_3)_2SO$ and $Pd(htbh)_2 \cdot 2(CH_3)_2SO$ it is evident that inter- and intra-molecular hydrogen-bonding involving $-OH$ of *o*-hydroxythiobenzhydrazide are responsible for crystallization of the complexes. The absence of –OH in other ligand moieties did not allow their complexes to crystallize. The spectral characters of Ni(htbh)$_2$ and Pd(htbh)$_2$ are similar to those of corresponding metal complexes of other ligands. Therefore it may be concluded that they also have similar structures.

Supplementary material

The spectral data of the complexes are available in the online version of this article as Supplementary material. CCDC Nos 693676 and 694279 contain the supplementary crystallographic data for [Ni(htbh)$_2$] · 2DMSO and [Pd(htbh)$_2$] · 2DMSO, respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK; Fax: (+44) 1223-336-033; or E-mail deposit@ccdc.cam.ac.uk.

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