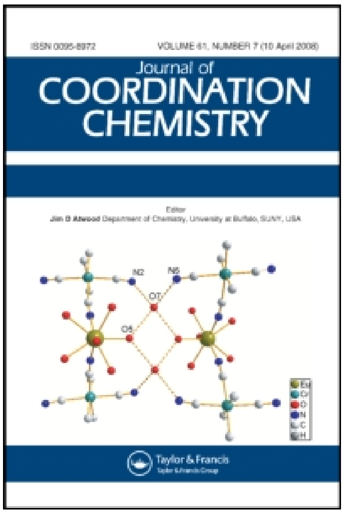

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Steric and electronic effects of <i>N</i>-coordinated NC^{-} and NCS$^-$ on NiS$_2$PN: synthesis, spectral and single crystal X-ray structural studies on <i>N</i>,<i>N</i>'-di-<i>n</i>-butyldithiocarbamate complexes of nickel(II) with phosphorus and nitrogen donor ligands

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Steric and electronic effects of *N*-coordinated NC^- and NCS^- on NiS_2PN: synthesis, spectral and single crystal X-ray structural studies on *N*,*N′*-di-*n*-butyldithiocarbamate complexes of nickel(II) with phosphorus and nitrogen donor ligands

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Planar nickel(II) complexes involving *N*,*N′*-dibutyldithiocarbamate, such as $[Ni(bu_2dtc)(PPh_3)(NC)]$ (**1**) and $[Ni(bu_2dtc)(PPh_3)(NCS)]$ (**2**) (where $bu_2dtc = N,N'$-dibutyldithiocarbamate anion) have been prepared, characterized by electronic, IR and NMR spectra and their structures determined by single crystal X-ray crystallography. Cyclic voltammetric characterizations of the complexes are also reported. IR spectra of the two complexes indicate the isobidentate coordination ($\nu_{\text{c-s}} \simeq 1095\,\text{cm}^{-1}$ without splitting) of the dithiocarbamate moiety. The important stretching mode characteristic of the thioureide bond ($\nu_{\text{C–N}}$) occurs at higher wave numbers compared to that of the parent dithiocarbamate complex $[Ni(bu_2dtc)_2]$. The electronic spectra of **1** and **2** show signature bands at 426 nm and 478 nm, respectively. NMR spectra show large ^{31}P chemical shifts in both compounds and the most important $N^{13}CS_2$ chemical shift appears at 204.86 ppm and 203.23 ppm for **1** and **2**, respectively. The CV studies clearly show the presence of reduced electron density on the nickel ions in mixed-ligand complexes **1** and **2** compared to the parent dithiocarbamate. Single crystal X-ray structure studies show that **2** crystallizes as a new triclinic polymorph, whose molecular structure closely resembles that of the previously reported monoclinic form. Both complexes contain a planar NiS_2PN chromophore in keeping with the observed diamagnetism. In both complexes the Ni-S distances are significantly different. The thioureide C–N distances of the complexes are shorter than those observed in the parent $[Ni(bu_2dtc)_2]$. The two compounds allow comparison of the influence of NCS^- in place of NC^-.

Keywords: Nickel(II); Dithiocarbamates; Cyanide-N; Thiocyanate-N; Thioureide; X-ray crystal structure

1. Introduction

Group X dithiocarbamato complexes with phosphines and nitrogen ligands have been in the limelight on account of their structural novelty and their biological profiles [1].

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Nickel(II) dithiocarbamates are typical planar complexes with NiS_4 chromophores, which are borderline acceptors which prefer to react with soft Lewis bases such as phosphines and hard bases such as nitrogen ligands [2]. The symbiotically induced softness and the electronic effects of the substituents on the dithiocarbamate ligands were found to be important in deciding the reactivity [3, 4]. Nickel(II) dithiocarbamates react with phosphines to form planar NiS_2P_2 chromophores which are diamagnetic [5, 6]. Synthetic and structural studies on $[Ni(dtc)(PPh_3)X]$ complexes, where $dtc = S_2CN(C_2H_5)_2^-$, $S_2CN(CH_3)(C_2H_4OH)^-$, $S_2CN(C_2H_4OH)_2^-$, $S_2CN(C_3H_7)_2^-$, $S_2CN(C_5H_{10})_2^-$ and X = Cl, SCN, CN, have been reported from our laboratory [7–10]. Unlike planar Pt(II) complexes, Ni(II) complexes do not stabilize their geometries effectively under various chemical environments for obvious reasons. For specialized applications under biochemical environments, it is advantageous to have planar Ni(II) complexes rather than their platinum analogues for reduced toxicity. To fine-tune an optimized stability for the NiS_2PN chromophore, different alkyl substituents on dithiocarbamates have been synthesized and analyzed. In our continuous efforts to investigate the synthetic and structural chemistry of NiS_2XY chromophores, where $X = Cl^-$ (or) SCN^- (or) CN^- and $Y = PPh_3$, we herein report the synthesis, spectral and single crystal X-ray structures of two complexes, $[Ni(bu_2dtc)(PPh_3)(NC)]$ (**1**) and $[Ni(bu_2dtc)(PPh_3)(NCS)]$ (**2**), where bu_2dtc = *N*,*N*′-di-*n*-butyldithiocarbamate.

2. Experimental

2.1. *Materials*

All reagents and solvents employed were commercially available analytical grade materials and were used as supplied without further purification.

2.2. *Preparation of (cyano-N)(di-n-butyldithiocarbamato)(triphenylphosphine)nickel(II) [Ni(bu₂dtc)(PPh₃)(NC)] (1)*

A mixture of $[Ni(bu_2dtc)_2]$ (0.12 g, 0.25 mmol), PPh_3 (0.13 g, 0.5 mmol), $NiCl_2\exists 6H_2O$ (0.06 g, 0.25 mmol) and KCN (0.033 g, 0.5 mmol) in acetonitrile-methanol (1:1 *v*/*v*, 50 cm^3) was refluxed for about 2 h followed by concentration to ca. 25 cm^3. The resultant orange yellow solution was left for evaporation. After two days, the orange yellow solid was filtered and dried over anhydrous calcium chloride. Single crystals suitable for X-ray structure analysis were obtained by recrystallization from the same solvent mixture (yield 70%, dec. 143°C). Anal. Calcd. (%) for $C_{28}H_{33}N_2NiPS_2$: C, 61.0; H, 6.0; N, 5.1. Found: C, 59.9; H, 5.7; N, 4.8%.

2.3. *Preparation of (di-n-butyldithiocarbamato)(thiocyanato-N)(triphenylphosphine) nickel(II) [Ni(bu₂dtc)(PPh₃)(NCS)] (2)*

A mixture of $[Ni(bu_2dtc)_2]$ (0.12 g, 0.25 mmol), PPh_3 (0.13 g, 0.5 mmol), $NiCl_2\exists 6H_2O$ (0.06 g, 0.25 mmol) and NH_4SCN (0.5 mmol) in acetonitrile-methanol (2:1 *v*/*v*, 50 cm^3) was refluxed for about 2 h followed by concentration to ca 25 cm^3. It was then left undisturbed for two days. The brownish red solid that separated from the solution was filtered and dried over anhydrous calcium chloride. Single crystals suitable for X-ray analysis were obtained by recrystallization from acetonitrile. (yield 80%, dec. 149°C). Anal. Calcd. (%) for $C_{28}H_{33}N_2NiPS_3$: C, 57.6; H, 5.7; N, 4.8. Found: C, 57.3; H, 5.5; N, 4.5%.

2.4. *Measurements*

IR spectra were recorded on an Avatar Nicolet FT-IR spectrophotometer (range $4000–400\,cm^{-1}$) as KBr pellets. The UV-visible spectra were recorded in CH_2Cl_2 on a Hitachi U-2001 double beam spectrophotometer. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AMX – 400 spectrophotometer at room temperature using $CDCl_3$ as solvent. Cyclic voltammetric measurements were carried out using an ECDA – 001 Basic Electrochemistry system. Glassy carbon was used as the working electrode and the counter electrode was platinum wire. The reference electrode was Ag|AgCl in lithium chloride in acetone. Tetrabutylammonium perchlorate (0.01 M) was used as the supporting electrolyte. The experiments were carried out under oxygen free atmosphere by bubbling purified nitrogen through the solution at room temperature.

2.5. *X-ray crystallography*

For both **1** and **2**, intensity data were collected on a Siemens AED diffractometer by using Cu-Kα radiation ($\lambda = 1.54178$ Å) and corrected for absorption with a psi-scan technique [11,12]. For **1**, the structure was solved by SHELXS-97 [13] and refined by SHELXL-97 [14]. During the refinement, some carbon atoms of the butyl chains showed unrealistically high thermal parameters indicating disorder, which was solved by splitting the C(3), C(4), C(5) and C(9) atoms over two positions. Refinement of a group site-occupancy factor for the major component converged to 0.700(11) for C(3), C(4), C(5) and to 0.812(9) for C(9). For **2**, the structure was solved by SIR97 [15] and refined by SHELXL-97 [14]. All hydrogen atoms of **1** and **2** were fixed geometrically with C–H distances in the range 0.93–0.97 Å and with $U_{iso}(H) = 1.2\ U_{eq}(C)$ or 1.5 $U_{eq}(C)$ for methyl hydrogen atoms. Molecular plots were obtained using the ORTEP-3 program [16].

Compound **2** is a new triclinic polymorph of $[Ni(bu_2dtc)(PPh_3)(NCS)]$, the other known polymorph being a $Z = 4$ phase crystallizing in the monoclinic space group $P2_1/c$ [17].

3. Results and discussion

3.1. *Crystal structures*

Crystal data and data collection parameters for **1** and **2** are shown in table 1. Selected bond distances and angles are given in table 2. An ORTEP diagram of $[Ni(bu_2dtc)(PPh_3)(NC)]$ is shown in figure 1. Structural analysis shows that the unit

Table 1. Crystal data, data collection and refinement parameters for $[Ni(bu_2dtc)(PPh_3)(NC)]$ and $[Ni(bu_2dtc)(PPh_3)(NCS)]$.

Compounds	$[Ni(bu_2dtc)(PPh_3)(NC)]$	$[Ni(bu_2dtc)(PPh_3)(NCS)]$
Empirical formula	$C_{28}H_{33}N_2NiPS_2$	$C_{28}H_{33}N_2NiPS_3$
Formula weight	551.36	583.45
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Crystal dimensions (mm^3)	$0.09 \times 0.13 \times 0.24$	$0.13 \times 0.15 \times 0.18$
a (Å)	9.883(2)	10.1465(4)
b (Å)	27.774(2)	11.3699(11)
c (Å)	10.381(2)	13.6290(7)
α (°)	90	83.791(7)
β (°)	95.30(2)	75.738(4)
γ (°)	90	76.202(8)
U (Å^3)	2837.3(8)	1477.83(17)
Z	4	2
D_c ($g\,cm^{-3}$)	1.291	1.3111
μ (mm^{-1})	3.026	3.577
$F(000)$	1160	612
λ (Å)	Cu-Kα (1.54178)	Cu-Kα (1.54178)
θ range (°)	3.18–70.01	3.35–70.10
Scan type	θ–2θ	θ–2θ
Index range	$-2 < h < 12$; $-33 < k < 33$; $-12 < l < 12$	$-12 < h < 3$; $-13 < k < 13$; $-16 < l < 16$
Reflections collected	5804	5620
Observed reflection $[F_o > 2\sigma(F_o)]$	4259	4400
Weighting scheme	$W = 1/[\sigma^2(F_o^2) + (0.1313P)^2]$ $P = (\max(F_o^2+2F_c^2)/3)$	$W = 1/[\sigma^2(F_o^2) + (0.0730P)^2 + (0.2763P)]$ $P = (\max(F_o^2+2F_c^2)/3)$
Number of parameters refined	321	317
Highest peak	0.62	0.71
Deepest hole	−0.49	−0.38
Final R, R_w (obs, data)	0.0524; 0.1676	0.0438; 0.1238
Goodness-of-fit	0.978	1.052

cell contains discrete mononuclear $[Ni(bu_2dtc)(PPh_3)(NC)]$ units with no significant intermolecular contacts. The Ni(1), S(1), S(2), P(1) and N(2) atoms are approximately coplanar [maximum displacement 0.069(3)Å for N(2)]. The planarity of the coordination around nickel(II) is also supported by the observed diamagnetism. The deviation of this plane from a perfect square is caused by the small bite angle [78.60(3)°] of the dithiocarbamate ligand. The two Ni–S bond distances, 2.2080(10)Å and 2.2121(9)Å, are significantly different. The Ni–S bond *trans* to NC^- is longer than that *trans* to *P* due to the different *trans* influences of phosphine and cyanide-N. The asymmetry in Ni–S bonds leads to an increase in Ni–S–C angles [86.47(10) and 86.06(11)°] and a decrease in S–C–S angle [108.86(16)°] compared to its parent dithiocarbamate [18]. The C–S bond lengths of 1.715(3)Å and 1.727(3)Å are intermediate between a theoretical C–S single- (1.81 Å) and double-bond lengths (1.69 Å), in agreement with the expected partial double-bond character [19]. The thioureide C–N distance [1.307(4)Å] is shorter than the corresponding distance in $[Ni(bu_2dtc)_2]$ [1.329(13)Å] [18], suggesting mesomeric drift of electron density from the dithiocarbamate toward the metal atom. The Ni–P and Ni–N distances are 2.1952(9)Å and 1.886(3)Å, respectively. The P–Ni–N angle [95.89(10)°] reflects the square planar coordination of the nickel atom. The deviation from linearity of the Ni–N–C angle [174.9(3)°] may be attributed to the steric effect of the

Table 2. Selected bond distances (Å) and angles (°).

Ni(1)–S(1)	2.2081(9)	2.216(1)
Ni(1)–S(2)	2.2121(10)	2.172(1)
Ni(1)–P(1)	2.1951(9)	2.205(1)
Ni(1)–N(2)	1.886(4)	1.861(2)
S(1)–C(1)	1.715(3)	1.696(3)
S(2)–C(1)	1.726(3)	1.719(4)
N(1)–C(1)	1.307(4)	1.307(5)
N(1)–C(2)	1.479(5)	1.475(6)
N(1)–C(6)	1.479(5)	1.529(5)
N(2)–C(10)	1.133(4)	1.149(4)
S(3)–C(10)		1.618(3)
P(1)–C(11)	1.822(3)	1.819(3)
P(1)–C(17)	1.830(3)	1.819(3)
P(1)–C(23)	1.824(3)	1.826(3)
S(1)–Ni(1)–S(2)	78.59(3)	78.36(3)
S(1)–Ni(1)–N(2)	91.15(10)	93.13(9)
S(2)–Ni(1)–P(1)	94.36(3)	91.73(3)
P(1)–Ni(1)–N(2)	95.89(10)	96.94(9)
S(1)–Ni(1)–P(1)	171.64(4)	168.89(4)
S(2)–Ni(1)–N(2)	169.74(19)	171.20(8)
Ni(1)–S(1)–C(1)	86.46(11)	86.03(10)
Ni(1)–S(2)–C(1)	86.07(11)	86.90(12)
S(1)–C(1)–S(2)	108.85(17)	108.5(2)
S(1)–C(1)–N(1)	125.5(3)	126.8(3)
S(2)–C(1)–N(1)	125.6(3)	124.6(2)
C(2)–N(1)–C(6)	117.3(3)	118.3(3)
Ni(1)–N(2)–C10	174.9(3)	171.3(3)
S(3)–C(10)–N(2)		179.7(3)
Ni(1)–P(1)–C(11)	111.30(9)	111.48(10)
Ni(1)–P(1)–C(17)	121.14(10)	109.64(10)
Ni(1)–P(1)–C(23)	110.44(10)	119.14(10)

phosphine ligand. The short N–C distance within the cyanide-N ligand [1.133(4)Å] indicates the characteristic triple bond. Phenyl rings show normal bond parameters. The observed average P–C distance is 1.825(3)Å. The C–P–C angles deviate appreciably from the normal tetrahedral angle and the resultant crowding of the phenyl rings causes the P–C–C angles to be asymmetric.

An ORTEP of $[Ni(bu_2dtc)(PPh_3)(NCS)]$ is shown in figure 2. Structural analysis shows that the unit cell contains discrete mononuclear units with no significant intermolecular contacts. The overall conformation of **2** closely resembles that reported for the monoclinic polymorph (hereafter referred to as (**2M**) [17]), with the exception of the mutual orientation of the butyl chains, one of which was found to be statistically distributed over two positions in (**2M**). The geometry of the NiS_2PN chromophore is tetrahedrally-distorted around the approximately square-planar nickel(II) ion [maximum displacement 0.094(3)Å for N(2)] because of small bite angle associated with the dithiocarbamate moiety [78.36(3)°]. The planarity of the coordination around the metal center is in keeping with the observed diamagnetism of the complex. The two Ni–S distances, 2.216(1)Å and 2.172(1)Å, are significantly different due to the different *trans* influences exerted by the phosphine and NCS^- ligands. Triphenylphosphine being a good π-acceptor exerts a greater *trans* influence and hence Ni–S bond *trans* to phosphine is longer than that *trans* to NCS^-. This feature is also observed in (**2M**), where the corresponding Ni–S bond lengths are 2.216(3) and 2.178(2)Å. The asymmetry

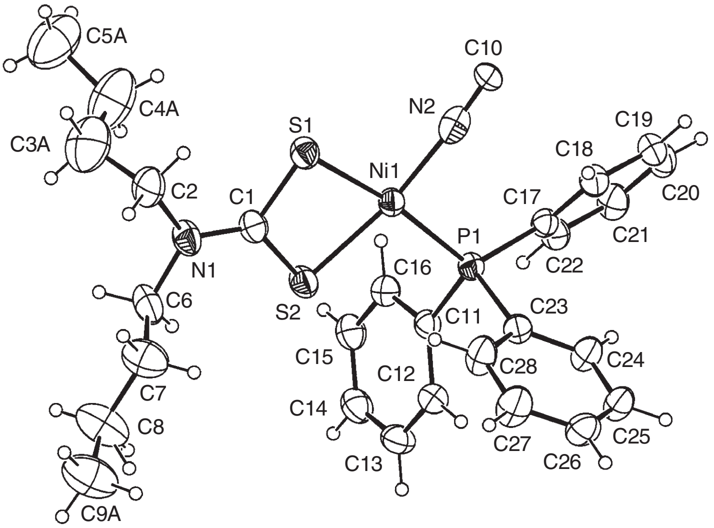

Figure 1. ORTEP diagram for [Ni(bu$_2$dtc)(PPh$_3$)(NC)] (**1**).

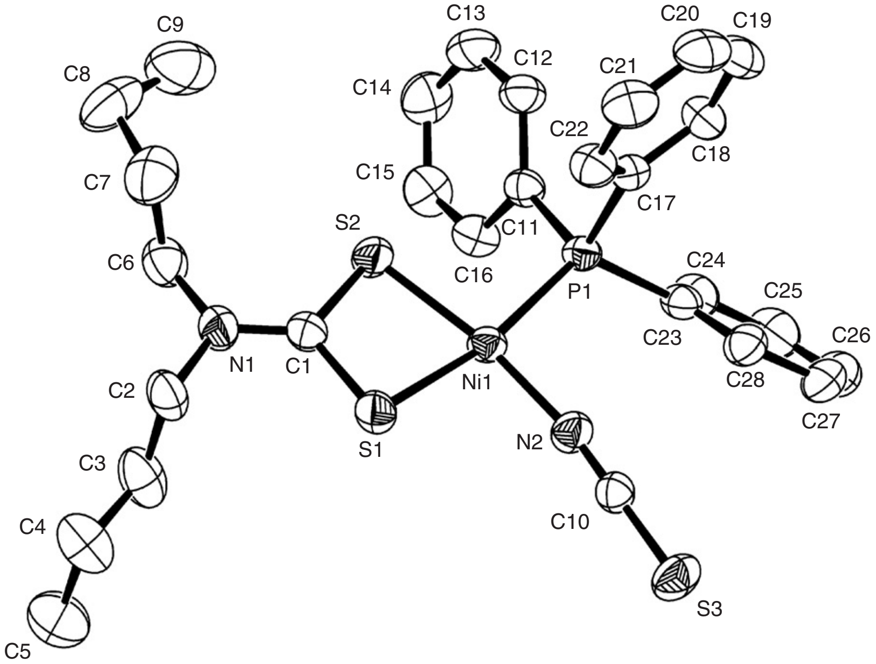

Figure 2. ORTEP diagram for [Ni(bu$_2$dtc)(PPh$_3$)(NCS)] (**2**).

in Ni–S bonds leads to an increase in the Ni–S–C angles [86.03(10)° and 86.90(12)°] and a contraction in the S–C–S angle [108.54(17)°], in agreement with the values determined in (**2M**) [Ni–S–C angles: 86.12(13) and 86.94(13)°; S–C–S angle: 108.3(2)°]. As observed in **1**, the values of the C–S bond lengths [1.696(3) and 1.719(4)Å] show

Table 3. Comparison of relevant bond distances (Å) and angles (°).

Complex	Ni–S(1)	Ni–S(2)	Ni–P	S(1)–C(1)	S(2)–C(1)	C(1)–N(1)	S–Ni–S	P–Ni–N	S–C–S
$Ni(bu_2dtc)_2$*	2.201(3)	2.211(3)	–	1.720(11)	1.742(11)	1.329(13)	79.4(1)	–	109.0(6)
1	2.2081(9)	2.2121(10)	2.1951(9)	1.715(3)	1.726(3)	1.307(4)	78.59(3)	95.89(10)	108.85(17)
2	2.172(1)	2.216(1)	2.205(1)	1.696(3)	1.719(4)	1.307(5)	78.36(3)	96.94(9)	108.5(2)

*Ref. [22].

partial double-bond character and are not significantly different from those found in (**2M**) [1.709(4) and 1.726(4)Å].

The short thioureide C–N distance [1.307(5)Å] indicates that the Π-electron density is delocalized over the S_2CN moiety and that this bond has strong double bond character. The Ni–N distance, 1.861(2)Å, is significantly longer than the distance reported for (**2M**) [1.850(3)Å] and for the octahedral $[Ni(en)_2(NCS)_2]$ compound (2.15Å [20]). The P–Ni–N angle [96.94(9)°] supports the planarity of the molecule.

The Ni–N–C angle [171.3(3)°; 170.8(3)° in (**2M**)] deviates from linearity as a result of the steric hindrance of the bulky triphenylphosphine ligand. The thiocyanate group is strictly linear, the N–C–S angle being 179.7(2)° [21]. The values of the C–N [1.149(4)Å] and C–S (1.618(3)Å) bond distances in NCS^- indicate their double-bond nature and are comparable with those of 1.161(4) and 1.617(4) Å quoted in (**2M**).

A comparison of relevant bond lengths and angles for **1** and **2** is given in table 3. Both complexes are asymmetric with respect to the Ni–S distances, attributed to different *trans* influences exerted by PPh_3, NCS^- and NC^-. The thioureide C–N distances in **1** and **2** are relatively shorter than in the parent compound. The decrease in the S–Ni–S bite angle for **1** and **2** compared to that of the parent dithiocarbamate [79.4(1)°] [18] is due to increase in steric crowding around the metal center.

The two compounds allow comparison of the influence of NCS^- and NC^-; both compounds have Ni–N coordination, but the bulky S-atom induces the following changes: (1) a significant increase in the Ni–P distance, (2) the P–Ni–N angle increases by 1°, (3) the Ni–N distance is shorter in **2** compared to **1** and (4) one of the N–C distances for a butyl chain shows a highly significant increase (N(1)–C(6): 1.529(5)). All these effects are due to the steric influence of sulfur. However, the Ni-S bond *trans* to Ni–N(CS) is significantly shorter than that involving Ni-N(C), indicating smaller *trans* influence of NCS^- compared to NC^-.

3.2. *Characterization*

Important IR absorptions in the dithiocarbamate complexes are due to $\nu_{C\text{–}N}$ and $\nu_{C\text{–}S}$ stretching modes. The $\nu_{C\text{–}N}$ band has been used as a measure of the contribution of the thioureide form to the structure of the dithiocarbamate compound. The IR spectra of **1** and **2** show thioureide ($\nu_{C\text{–}N}$) bands at 1525 and 1530 cm^{-1}, respectively. The shift in $\nu_{C\text{–}N}$ bands to higher frequencies compared to the parent $[Ni(bu_2dtc)_2]$ (1506 cm^{-1}) is due to the mesomeric drift of electron density from the dithiocarbamate moiety towards the nickel ions. The $\nu_{C\text{-}S}$ bands appear at 1096 and 1095 cm^{-1} for **1** and **2**, without splitting, supporting the isobidendate coordination of the dithiocarbamate moiety [22]. IR spectra also show bands at 2112 and 2096 cm^{-1} for **1** and **2**, respectively. The band at 2112 cm^{-1} in **1** indicates the presence of a N-coordinated cyanide ion. The strong band at 2096 cm^{-1} in **2** corresponds to the N-coordinated thiocyanate [23].

In all the nickel(II) complexes, bands below 350 nm in UV visible spectra are due to intraligand π–π^* transitions, mainly associated with the N–C = S and S–C = S groups. Several authors ascribe intense bands in the 350–425 nm region to either metal-ligand or ligand-metal charge transfer [24]. In addition to these charge transfer bands, electronic spectral bands in the range 425 to 650 nm are due to d–d transitions [25]. The parent dithiocarbamate $[Ni(bu_2dtc)_2]$ shows weak bands at 469 and 628 nm due to $d_z^2 \rightarrow d_x^2 - d_y^2$ and $d_{xy} \rightarrow d_x^2 - d_y^2$ transitions, respectively. Of the two bands shown by the parent, the one at 628 nm shifts to higher wavelength in the mixed ligand complexes. Only the 469 nm band appears clearly in the mixed ligand complexes. Electronic spectra of **1** and **2** show bands at 426 and 478 nm, respectively. The least λ_{max} value associated with **1** is due to cyanide exerting a larger LFSE. Charge transfer bands are observed below 400 nm. Electronic spectral data of the complexes support the assumption of square planar geometry around nickel in both complexes.

CV studies indicate that **1** and **2** undergo a one-electron reduction process $[Ni(II) \rightarrow Ni(I)]$ with lower reduction potential (−1338 and −1040 mV, respectively) than the parent $[Ni(bu_2dtc)_2]$ (−1752 mV), showing reluctance to add more electron density to the already electron rich metal center in the parent complex. The more negative reduction potential of **1** indicates the presence of more electron density on **1** compared to **2**.

The ^1H, ^{13}C and ^{31}P NMR chemical shifts are given in table 4. For **1** and **2** the butyl groups are non-equivalent and hence α, β and γ-methylene protons and terminal methyl protons give only broad signals, indicating a substantial barrier to C–N bond rotation. The α-methylene protons adjacent to the nitrogen atom undergo strong deshielding at 3.3–3.6 ppm, whereas the signal for terminal methyl protons is at 0.85–0.94 ppm. The aromatic protons from triphenylphosphine resonate in the region of 7.25–7.74 ppm in both complexes.

The ^{13}C chemical shifts of the thioureide carbon atom are correlated to π-bonding in the NCS_2^- fragment [9]. Generally, higher $\nu_{C\text{-}N}$ values correlate with lower $N^{13}CS_2$ ppm values for d-block elements. The chemical shifts of the thioureide carbon ($N^{13}CS_2$) are observed at 204.8 and 203.2 ppm for **1** and **2** [26]. This is due to the alleviation of excess electron density on nickel by phosphine, cyanide-N, and thiocyanate-N, which results in drift of electron density towards the metal through the thioureide bond from the nitrogen atom, supporting the bidentate coordination of the dithiocarbamate and

Table 4. NMR spectral data (chemical shifts in ppm).

Complex	NMR	PPh_3	CH_3	γ-CH_2	β-CH_2	α-CH_2	$N^{13}CS_2$	NCS/NC
$[Ni(bu_2dtc)(PPh_3)(NC)]$ **1**	^1H	7.25–7.74	0.85–0.94	1.22–1.35	1.50–1.70	3.40–3.60		
	^{13}C	134.8–128.5	13.5	19.8	29.2	48.2–49.1	204.8	130.7
	^{31}P	29.91						
$[Ni(bu_2dtc)(PPh_3)(NCS)]$ **2**	^1H	7.26–7.72	0.86–0.94	1.34–1.49	1.59–1.72	3.33–3.52		
	^{13}C	134.1–128.1	13.5	19.7	29.1	48.9	203.2	143.0
	^{31}P	22.27						

^1H and ^{31}P NMR chemical shifts are listed to ±0.01 ppm and the ^{13}C chemical shifts to ±0.1 ppm accuracy.

strong back bonding. The thiocyanate-N has higher back bonding ability, and hence **2** shows a signal in the upfield region (203.2 ppm). The cyanide-N carbon atom and thiocyanate-N carbon atom chemical shifts appear at 130.7 and 143.0 ppm, respectively. The chemical shift of cyanide merges with those of the phosphine phenyl rings in the region 128–135 ppm. In the *n*-butyl chain, the α-methylene carbon appears to be deshielded to a greater extent and signals are observed around 48 ppm for **1** and **2**. The terminal methyl carbon signals are observed in the upfield region (13.5 ppm) relative to the γ-CH_2 carbon signals (19.8 ppm) in both complexes.

^{31}P NMR spectra of **1** and **2** show signals assignable to the coordinated phosphorous atoms at 29.91 and 22.27 ppm, respectively; free PPh_3 resonates at -5.8 ppm [22]. The deshielding for coordinated phosphorus in **1** and **2** indicates drift of electron density from phosphorus towards the metal and hence strong coordination.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Collection Centre: deposition number(s) CCDC 602828 and 626217 for (**1**) and (**2**), respectively. Copies of the data can be obtained free of charge on request quoting the deposition number from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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