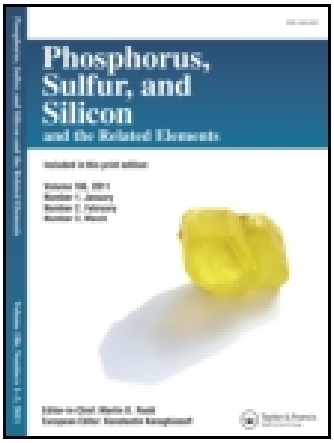

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Synthesis and Characterization of Homoleptic and Heteroleptic Complexes Involving Dithiocarbamates, Triphenylphosphine, and Nickel(II)

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SYNTHESIS AND CHARACTERIZATION OF HOMOLEPTIC AND HETEROLEPTIC COMPLEXES INVOLVING DITHIOCARBAMATES, TRIPHENYLPHOSPHINE, AND NICKEL(II)

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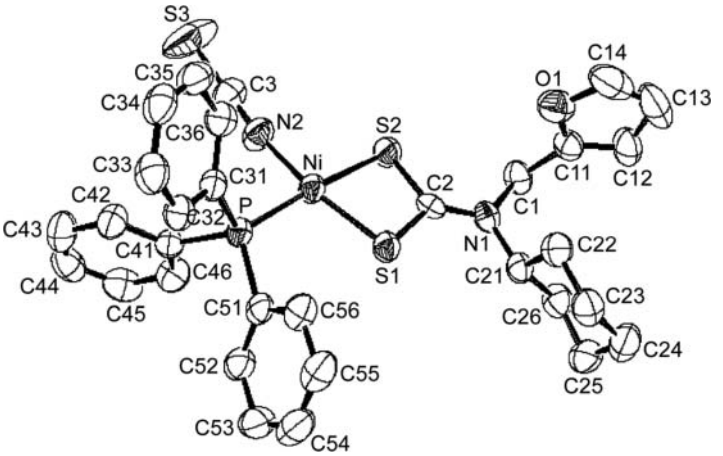
GRAPHICAL ABSTRACT



Abstract *Six new nickel complexes of two dithiocarbamate ligands (cyfdtc = N-cyclohexyl-N-furfuryldithiocarbamate and bztpedtc = N-benzyl-N-[2-thiophenylethyl]dithiocarbamate) namely, (Ni[cyfdtc]$_2$) (**1**), (Ni[bztpedtc]$_2$) (**2**), (Ni[cyfdtc][NCS][PPh$_3$]) (**3**), (Ni[bztpedtc][NCS][PPh$_3$]) (**4**), (Ni[cyfdtc][PPh$_3$]$_2$)ClO$_4$ (**5**), and (Ni[bztpedtc][PPh$_3$]$_2$)ClO$_4$ (**6**) have been prepared and characterized using IR, electronic, and NMR (^{1}H and ^{13}C) spectra. A single crystal X-ray structural analysis was carried out for complex **3** and showed that nickel is in a distorted square planar arrangement with the NiS$_2$PN chromophore. The shift in ν_{C-N} of the heteroleptic complexes to higher frequencies compared with the parent complex is assigned to mesomeric delocalization of electron density from the*

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*dithiocarbamate ligand toward the metal atom, which increases the contribution of polar thioureide form in mixed ligand complexes. Electronic spectral studies suggest square planar geometry for the complexes. In the ^{13}C NMR spectra, the upfield shift of NCS_2 carbon signal for **3** and **4** from the chemical shift value of **1** and **2** is due to effect of PPh_3 on the mesomeric drift of electron density toward nickel throughout thioureide C—N bond.*

Keywords Dithiocarbamate; triphenylphosphine; nickel(II); spectral; X-ray structure

INTRODUCTION

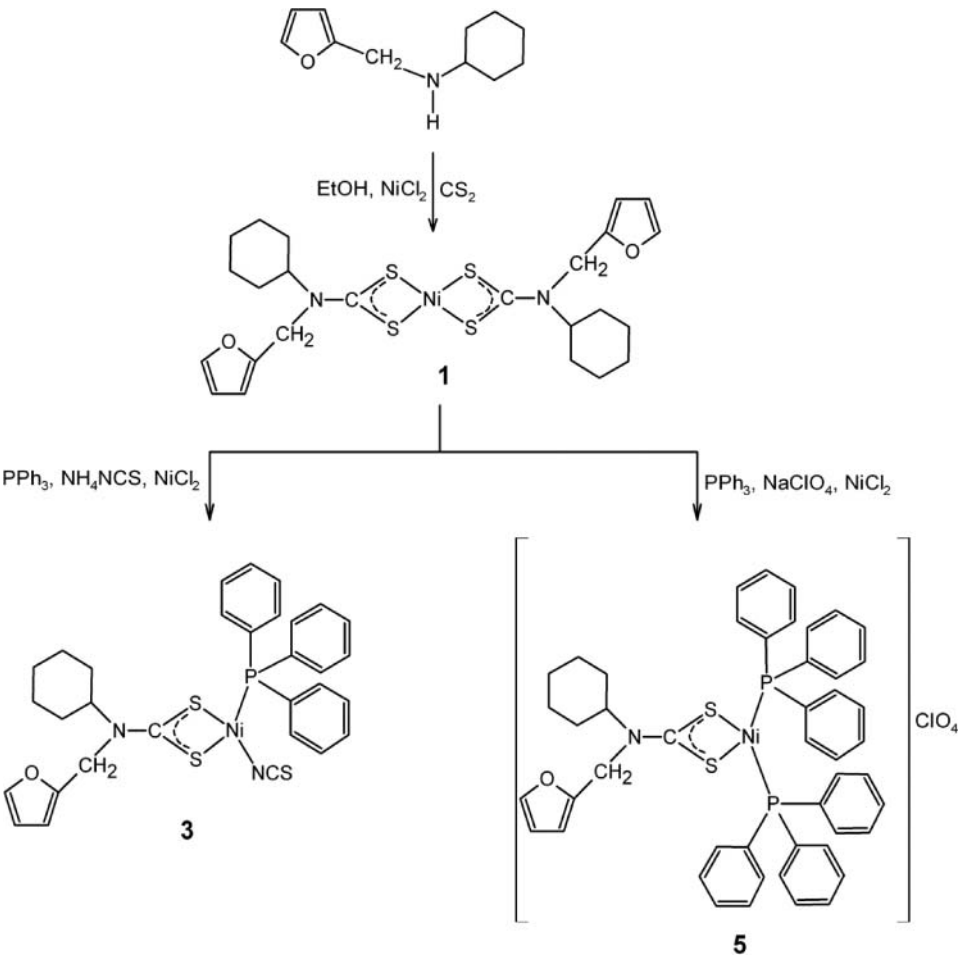
The coordination chemistry of complexes containing sulfur donor ligands has been steadily growing due to their resemblance with biomolecules like amino acids (e.g., methionine, cystein), peptides such as glutathione, proteins, enzymes, and vitamins.[1] Among the various organosulfur systems, dithiocarbamates have special significance due to their wide applications such as potential pesticides, in analytical determinations, and as fungicides and vulcanizing agents.[2–4] The versatility of dithiocarbamato ligands may be attributed to their small bite angle, leading to the stabilization of a wide range of oxidation states of transition metal and main group elements.[5,6] The complexing ability of dithiocarbamato ligands stems from the presence of the potential sulfur donors, which can delocalize positive charge from the metal toward the periphery of the complex.[7] These dithiocarbamato complexes have been shown to be useful precursors for formation of metal sulfide nanoparticles.[8–10] Recently, dithiocarbamates have also been used as structural motifs in the supramolecular chemistry due to their robust complexing ability.[11]

The diversity in applications inherent to nickel(II) complexes with homoleptic and chelating phosphine as catalysts[12–14] and in the medicinal field,[15] combined with their structural novelty, has resulted in the synthesis of a series of compounds with NiP_nX (X = halogens or N or C or S) chromophores. Nickel(II) dithiocarbamates with a planar NiS_4 chromophores are found to show interesting variations in reactivity toward soft Lewis bases such as phosphines and hard bases such as nitrogenous ligands.[16,17]

The dithiocarbamate complex core $M—S_2CNR_2$ (M = metal, R = alkyl) could prove to be of great synthetic utility, since a wide variety of organic substituents can be incorporated in this stable bidentate system. It gives rise to the chemical "fine tuning" of the biological properties of the complex by variation of the substituent R in $M—S_2CNR_2$.[18] The aim of the present work was to prepare Ni(II) complexes of two unsymmetrical dithiocarbamate ligands with furfuryl and 2-thiophenylethyl substituents and the reactivity of these complexes toward PPh_3. In this paper, we report the synthesis and spectral studies of complexes **1–6** along with the single crystal X-ray structure of **3**.

RESULTS AND DISCUSSION

Homoleptic and heteroleptic complexes were prepared according to the synthetic procedure shown in Schemes 1 and 2. Furfuraldehyde and benzaldehyde were condensed with cyclohexylamine and thiophenethylamine, respectively, to form the imine. Sodium borohydride reduction of the imine in methanol–dichloromethane afforded the secondary amine as yellow oil. The homoleptic $[Ni(dtc)_2]$ complexes of **1** and **2** were prepared from a secondary amine in EtOH by reaction with carbon disulfide and $NiCl_2$ in water. The reaction under continued reflux (3 h) between $[Ni(dtc)_2]$, $NiCl_2$, NH_4SCN, and PPh_3 yielded $[Ni(dtc)(NCS)(PPh_3)]$ (**3** and **4**). $[Ni(dtc)(PPh_3)_2]ClO_4$ (**5** and **6**) complexes were prepared by refluxing $[Ni(dtc)_2]$, $NiCl_2$, $NaClO_4$, and PPh_3 in chloroform–methanol (3:2,

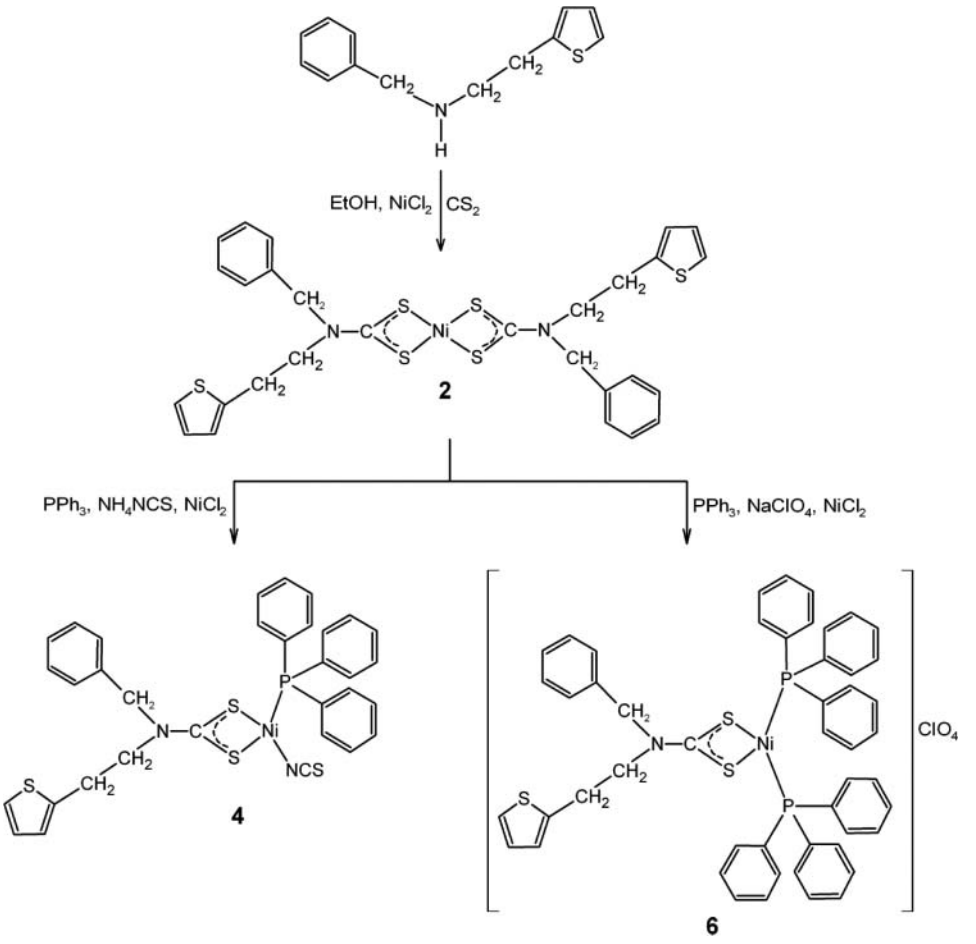


Scheme 1 Preparation of complexes **1**, **3**, and **5**.

50 mL) mixture. The complexes are quite stable at ambient conditions. They are soluble in acetonitrile, chloroform, and dichloromethane and insoluble in water, methanol, and ethanol.

IR Spectra

The infrared spectra of dithiocarbamato complexes consist of two characteristic bands, which are of direct structural significance. The first lies in the region 950–1050 cm^{-1}, which exhibits the nature of coordination mode (monodentate or bidentate) of the dithiocarbamate moiety[19] while the second lies in between 1450–1600 cm^{-1} and is termed the thioureide band.[20] This thioureide band may be considered as an intermediate between single- and double-bonded C—N and its position indicates the shift of electron density toward the coordinating metal ion. Based on Bonati and Ugo[21] criterion, the presence of a solitary band in the 950–1050 cm^{-1} region is due to the bidentate coordination of the dithiocarbamato group while the splitting of this band within narrow range of 20 cm^{-1} is due to the monodentate nature of the dithiocarbamato group.



Scheme 2 Preparation of complexes **2**, **4**, and **6**.

The infrared spectra of **1–6** show ν_{C-N}(thioureide) bands in the region 1461–1502 cm^{-1}, indicating the partial double bond character. In the case of heteroleptic complexes, the ν_{C-N} values were found to be larger than those of the parent dithiocarbamates. This observation shows the increased strength of the thioureide bond due to the presence of π-accepting phosphine. In the present study, the ν_{C-S} stretching vibrations are observed in the region 1011–1025 cm^{-1} without any splitting, supporting the bidentate coordination of the dithiocarbamate ligand. The bands observed around 2090 ($\nu_{C\equiv N}$) and 840 cm^{-1} (ν_{C-S}) for the complexes **3** and **4** may imply the assumption that the thiocyanate group is coordinated to the nickel via the nitrogen atom.[22] The intense signals observed around 1090 cm^{-1} for **5** and **6** are assigned to ClO_4^-.

Electronic Spectra

Dithiocarbamates generally show three bands in the UV region. These bands are ascribed to the intramolecular intraligand transitions corresponding to $\pi \rightarrow \pi^*$ transitions

of the N—C=S and S—C=S groups and $n \rightarrow \pi^*$ transition located on the sulfur atom.[23] In the case of **1** and **2**, two *d–d* transition bands are observed around 630 and 487 nm corresponding to the $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions, respectively, supporting a square-planar structure.[24] The *d–d* transition bands are observed at 487, 487, 480, and 485 nm for complexes **3**, **4**, **5** and **6**, respectively. The bands are assigned to $d_{z^2}/d_{xy} \rightarrow d_{x^2-y^2}$ transitions.[17]

^{1}H NMR Spectra

^{1}H NMR spectra of **2** and **4** are given in Figure 1 to show single broad signal and broad doublets observed for each methylene proton in **2** and **4**, respectively. Free N-cyclohexyl-N-furfurylamine shows a singlet at 3.78 ppm and a broad signal at 2.42 ppm due to methylene protons of furfuryl and methine proton of cyclohexyl groups, respectively. In the complexes **1**, **3**, and **5**, the methylene protons of furfuryl and methine proton of cyclohexyl

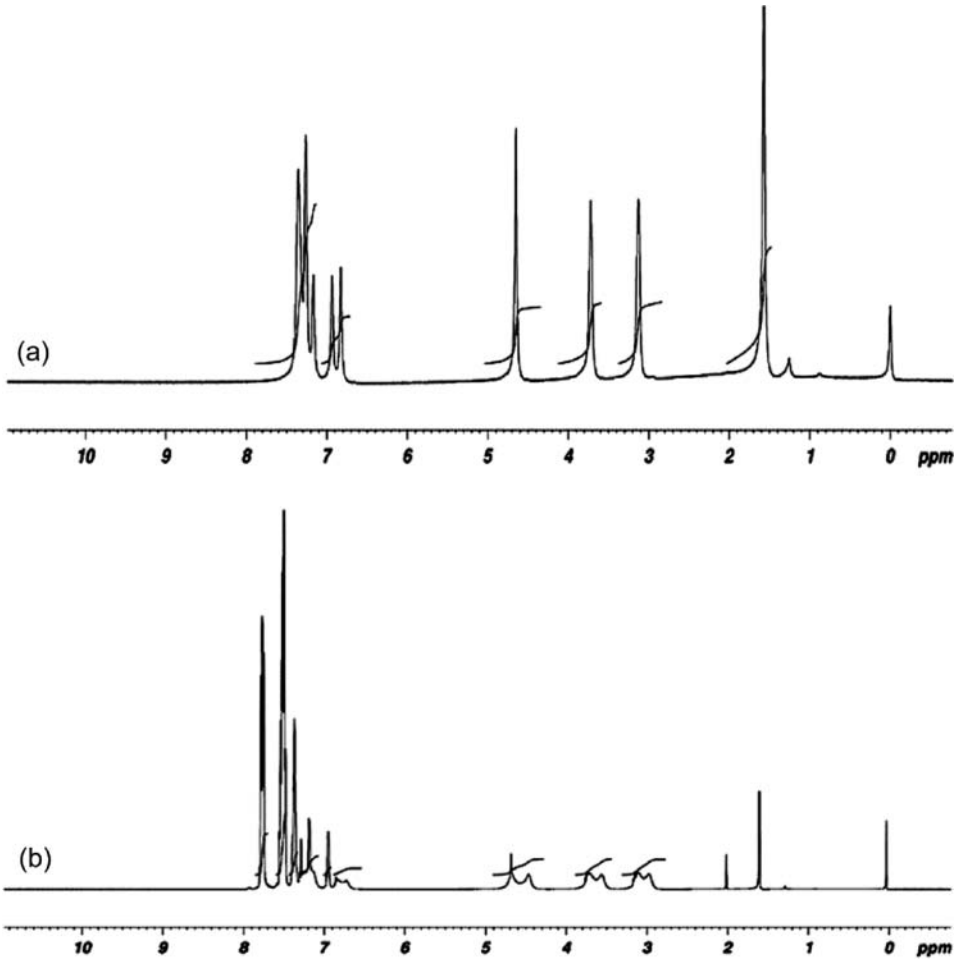


Figure 1 ^{1}H NMR spectra of (a) **2** and (b) **4**.

group, adjacent to N-atom, undergo strong deshielding to give the signals around 4.74 and 4.41 ppm, respectively. Similarly, in the case of complexes **2**, **4**, and **6**, the benzyl methylene protons (4.69 ppm) of benzyl group and methylene protons (3.73 ppm) of thiophenylethyl group, adjacent to nitrogen atoms, are strongly deshielded on complexation compared to free N-benzyl-N-(2-thiophenylethyl)amine [3.66 ppm (NCH_2(benzyl)) and 2.92 ppm (NCH_2(thiophenylethyl))]. The observed deshielding of methylene and methine protons adjacent to nitrogen atom is attributed to the release of electrons on the nitrogen of the NR_2 groups, forcing high electron density toward the sulfur (or) the metal via the thioureide π-system. The magnitude of deshielding decreases with an increase in distance from the metal center or thioureide bond, the other proton signals are also slightly deshielded on complexation.

In the case of **3**, the signals due to furfuryl $-CH_2$ protons and cyclohexyl methine protons appear as broad doublets. Similarly, the methylene protons adjacent to the nitrogen of bztpedtc in heteroleptic complexes **4** (Figure 1) and **6** are observed as broad doublets. This is due to the ligand exchange reactions as observed in [Ni($SCNEt_2$)(PPh_3)X] (X = Cl, Br, I, NCS) complexes.[25]

^{13}C NMR Spectra

^{13}C NMR spectrum of **3** is given in Figure 2 to show the pseudo doublets observed for methylene and methine carbons adjacent to nitrogen atom of **3**. The most important ^{13}C NMR signals of the $S_2{}^{13}CN$ carbons are observed in the region 205.3–208.9 ppm for [Ni($dtc)_2$] and [Ni(dtc)(NCS)(PPh_3)] with a very weak intensity characteristic of the quaternary carbon signals. The $S_2{}^{13}CN$ carbon signal for **3** and **4** is observed at 205.3 and 205.7 ppm, respectively, with an upfield shift of about 3.5 ppm, respectively, compared

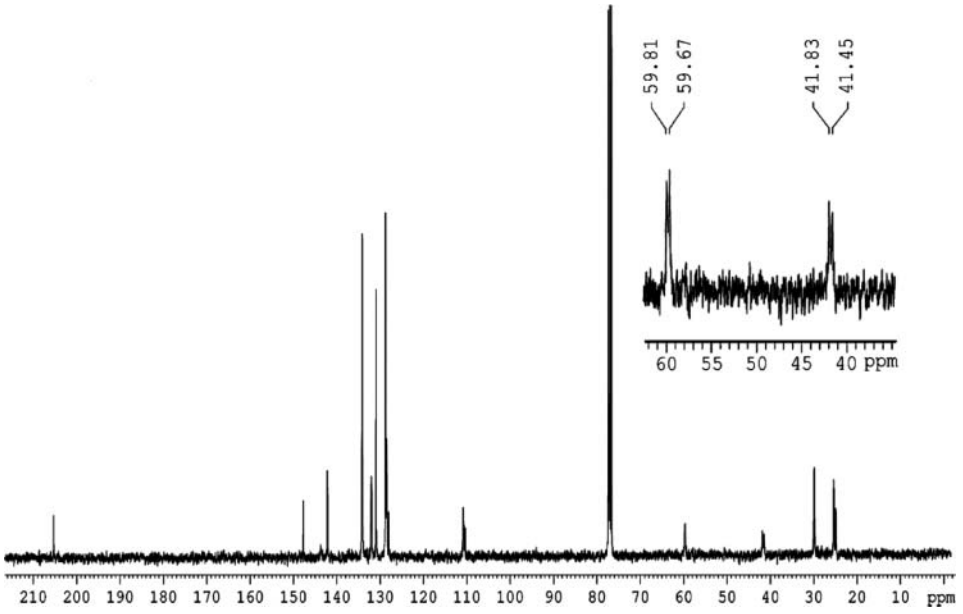


Figure 2 ^{13}C NMR spectrum of **3**.

with that found in parent **1** (208.8 ppm) and **2** (208.9 ppm). The presence of π-acid (triphenylphosphine) in [Ni(dtc)(NCS)(PPh_3)] increases the mesomeric drift of electron density from the dithiocarbamate moiety toward the metal atom. This yields an increase in the $N^{\delta+} \cdots C^{\delta-}$ partial double bond character, and as a result, displacement of the electron density from the nitrogen atom of the dithiocarbamate group.[22] This explains the shielding of carbon sites in the −N−C(S)S group of [Ni(dtc)(NCS)(PPh_3)]. Most of the dithiocarbamate signal in the ^{13}C NMR spectra of mixed ligand complexes appeared as *pseudo* doublets. This is consistent with the square planar geometry for the complexes. Doublets or *pseudo* triplets are also observed in triphenylphosphine transition metal complexes.[26]

Crystallographic Analysis of Complex 3

Complex **3** is discrete and monomeric. Four formula units are present in the unit cell. The ORTEP diagram is shown in Figure 3. The structure consists of distorted square planar metal coordination with NiS_2PN chromophore. The structure adopted by this complex is characterized using τ_4-descriptor for four coordination ions suggested by Yang et al.[27] The distortion index is defined as $\tau_4 = 360–(\alpha+\beta)/141$. In this complex, α and β are the two largest angles (N2−Ni−S1 = 171.97° and P−Ni−S2 = 174.97°). The τ_4 values for perfect tetrahedral, trigonal pyramid, seesaw structure, and perfect square planar are 1.00, 0.85, 0.64–0.07, and 0.00, respectively. The τ_4 value of this complex is 0.09, which indicates that the coordination geometry is a seesaw structure. There are considerable differences between the pairs of Ni−S and S−C bonds and it is interesting to note that the longer Ni−S bond [Ni−S2 = 2.213(8) Å compared with Ni−S1 = 2.1677(8) Å] is associated with shorter S−C distance (S2−C2 = 1.716[3] Å compared with S1−C2 = 1.733[3] Å). This indicates that the dithiocarbamate ligand is asymmetrically linked to nickel. The significant asymmetry in Ni−S distance is due to the difference in the *trans*-influencing properties of PPh_3 and NCS^-. Ni−S bond *trans* to PPh_3 is longer than the other Ni−S bond. This observation supports the more effective *trans* effect of PPh_3 over NCS^-. The asymmetric C−S distances are shorter than the typical C−S single bond length (1.81 Å) due to the partial π-delocalization in the NCS_2 groups.[6] The C−N distance (1.303[3] Å), which clearly indicates the contribution of the thioureide form to the dithiocarbamate ligand. This contrasts well with the adjacent typical single bond N−C distance (1.485[3] Å).

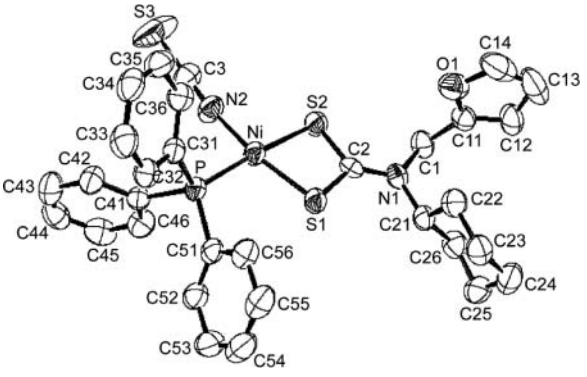


Figure 3 ORTEP diagram of **3**.

In the isothiocynate part, the N—C—S is almost linear [N—C—S = 179.3(3)°]. . The Ni—N distance is 1.856(2) Å, which is similar to that observed in similar [Ni(dtc)(NCS)(PPh_3)] complexes.[28] The observed Ni—P distance (2.1977[8] Å) is relatively short compared to a long Ni—P = 2.40 Å bonded distance reported in the literature.[29] The cyclohexyl ring in the dithiocarbamate fragment is in the chair conformation. The C—C and C—O bond distances associated with furfuryl ring are normal. The bond lengths and angles in the phenyl rings are in good agreement within experimental accuracy, with the values found in the literature.[30]

CONCLUSIONS

New complexes [Ni(dtc)$_2$], [Ni(dtc)(NCS)(PPh_3)], and [Ni(dtc)(PPh_3)$_2$]ClO_4 (dtc = cyfdtc, bztpedtc) have been synthesized and characterized through elemental analysis and spectroscopic studies. The spectral studies on complexes **1–6** indicate that the central metal atom is in a planar environment for all complexes. Single crystal X-ray analysis of **3** confirmed that the nickel is in a distorted square planar environment with S_2PN chromophore. A significant asymmetry in the Ni—S bond in **3** [2.1677(8) and 2.2131(8) Å] supports the less effective *trans* effect of NCS— over PPh_3.

EXPERIMENTAL

All reagents and solvents were commercially available high-grade materials (Merck/sd Fine/Himedia) and used as received. IR spectra were recorded on a Thermo NICOLET AVATAR 330 FT-IR spectrophotometer (range 400–4,000 cm^{-1}) as KBr pellets. A Shimadzu UV-1650 PC double beam UV-visible spectrophotometer was used for recording the electronic spectra. The spectra were recorded in $CHCl_3$ and the pure solvent was used as the reference. The NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer at room temperature (r.t.) in $CDCl_3$, using TMS as internal reference.

X-Ray Crystallography

Diffraction data for **3** were recorded on an Xcalibur-3/CCD diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71069 Å) at an ambient temperature. The structure was solved by SHELXS[31] and refined by full-matrix least-squares methods in SHELXL.[31] All the nonhydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. Details of the crystal data and structure refinement parameters for **3** are summarized in Table 1. Selected bond distances and angles are presented in Table 2.

Preparation of Amine

N-Cyclohexyl-N-furfurylamine and N-benzyl-N-(2-thiophenylethyl)amine were prepared by general methods reported earlier.[32]

Preparation of Complex 1

N-Cyclohexyl-N-furfurylamine (0.7 mL, 4 mmol) and carbon disulfide (0.3 mL, 4 mmol) were dissolved in ethanol (20 mL) and stirred for 30 min. $NiCl_2 \cdot 6H_2O$ (0.57 g,

Table 1 Crystal structure and data refinement parameters for **3**

Empirical formula	$C_{31}H_{31}N_2OPS_3Ni$
FW	633.44
Crystal dimensions (mm)	0.2 × 0.2 × 0.2
Crystal system / Space group	Monoclinic/$P2_1/c$
a (Å)	8.9130(10)
b (Å)	20.0970(10)
c (Å)	17.3590(10)
α (°)	90.000(5)
β (°)	98.193(5)
γ (°)	90.00
V (Å^3)	3077.7(4)
Z	4
Dc (g cm^{-3})	1.367
μ (cm^{-1})	0.913
Crystal size (mm)	0.2 × 0.2 × 0.2
Colour/shape	Dark red/Prism
Temp. (K)	293(2)
Theta range for collection	4.45–26.40
Reflections collected	15216
Independent reflections	6077
Data/restrains/parameters	4011/0/352
Goodness of fit on F^2	1.041
Final *R* indices ($I > 2\sigma$[I])	$R_1 = 0.0439$, $wR_2 = 0.0929$
R indices (all data)	$R_2 = 0.0773$, $wR_2 = 0.1000$
Largest difference peak/hole (eÅ^{-3})	0.436–0.387

2 mmol) was dissolved in 10 mL of water and added to the solution with constant stirring. A green powder precipitated that was filtered and dried.

Yield: 70%. mp 300 °C. IR (KBr, cm^{-1}) 1461 (ν_{C-N}), 1011 (ν_{C-S}), 2937, 2854 ($\nu_{C-H(aliph.)}$). UV-Vis ($CHCl_3$, λ_{max}/nm (ε/L mol^{-1} cm^{-1})): 622 (115), 481 (190), 371 (7350), 235 (35700). ^{1}H NMR (ppm): $\delta = 1.09$ (b, 2H, H–4 (ax)), 1.30–1.43 (m, 8H, H–3), 1.64 (d, $J = 17$ Hz, 2H, H–4 (eq)), 1.78 (b, 8H, H–2), 4.44 (b, 2H, H–1), 4.74 (s, 4H, NCH_2 (furfuryl)), 6.33 (b, 2H, H–4 (furyl)), 6.40 (b, 2H, H–3 (furyl)), 7.34 (b, 2H, H–5 (furyl)). ^{13}C NMR (ppm): $\delta = 25.2$ (C–4), 25.6 (C–3), 30.0 (C–2), 41.4 (NCH_2 (furfuryl)), 59.2 (C–1), 110.0, 110.8, 141.8, 148.7 (Aryl–C (furyl)), 208.8 (SCS). Anal. Calcd. for $C_{24}H_{32}S_4N_2O_2Ni$ (%): C, 50.79; H, 5.68; N, 4.93. Found (%): C, 50.45; H, 5.52; N, 4.80.

Table 2 Selected bond distances (Å) and angles (°) for **3**

Bond distances (Å)		Bond angles (°)	
Ni−N2	1.856(2)	N2−Ni−S1	171.97(8)
Ni−P	2.1977(8)	N2−Ni−P	91.91(8)
Ni−S1	2.1677(8)	S1−Ni−P	96.04(3)
Ni−S2	2.2131(8)	N2−Ni−S2	93.09(8)
S1−C2	1.733(3)	S1−Ni−S2	78.95(3)
S2−C2	1.716(3)	P−Ni−S2	174.97(3)
S3−C3	1.607(3)	Ni−C2−S1	125.4(2)
N2−C3	1.343(3)	Ni−C2−S2	126.8(2)

Preparation of Complex 2

The same procedure was used as earlier except that N-benzyl-N-(2-thiophenylethyl)amine was used instead of N-cyclohexyl-N-furfurylamine.

Yield: 75%. mp 210 °C. IR (KBr, cm^{-1}) 1501 (ν_{C-N}), 1021 (ν_{C-S}), 2923, 2853 ($\nu_{C-H(aliph.)}$), 3020 ($\nu_{C-H(arom.)}$). UV-Vis ($CHCl_3$, λ_{max}/nm (ε/L mol^{-1} cm^{-1})): 630 (153), 487 (401), 398 (1980). ^{1}H NMR (ppm): $\delta = 3.13$ (b, 4H, N$-CH_2-$C$\underline{H}_2-C_4H_3S$), 3.72 (b, 4H, NC$\underline{H}_2-CH_2-C_4H_3S$), 4.65 (b, 4H, NC$\underline{H}_2$ (benzyl)), 6.83–7.36 (Aryl−H). ^{13}C NMR (ppm): $\delta = 27.4$ ($NCH_2-\underline{C}H_2-C_4H_3S$), 50.2 (N$-\underline{C}H_2-CH_2-C_4H_3S$), 52.8 ($NCH_2$ (benzyl)), 124.4–139.6 (Aryl−C), 208.9 (SCS). Anal. Calcd. for $C_{28}H_{28}S_6N_2Ni$ (%): C, 52.25; H, 4.38; N, 4.35. Found (%): C, 51.78; H, 4.29; N, 4.31.

Preparation of Complex 3

A mixture of complex **1** (0.56 g, 1.0 mmol), PPh_3 (0.52 g, 2 mmol), $NiCl_2{\cdot}6H_2O$ (0.327 g, 1.0 mmol), and NH_4NCS (0.152 g, 2.0 mmol) was refluxed for 3 h in chloroform–methanol solvent mixture (3:2, 50 mL). The purple red solution obtained was filtered and left for evaporation. After 2 days, a purple red solid separated out, which was recrystallized from chloroform. Suitable single crystals for X-ray structure analysis were obtained by repeated crystallization from dichloromethane—methanol solvent mixture.

Yield: 65%. mp 240 °C. IR (KBr, cm^{-1}) 1485 (ν_{C-N}), 1011 (ν_{C-S}), 2089 (NCS), 2931, 2857 ($\nu_{C-H(aliph.)}$), 3053 ($\nu_{C-H(arom.)}$). UV-Vis ($CHCl_3$, λ_{max}/nm (ε/L mol^{-1} cm^{-1})): 487 (5640), 336 (98600), 240 (362000). ^{1}H NMR (ppm): $\delta = 1.06$ (b, 1H, H–4 (ax)), 1.35–1.43 (m, 4H, H–3), 1.61 (b, 1H, H–4 (eq)), 1.74 (b, 4H, H–2), 3.98, 4.35 (b, 1H, H–1), 4.52, 4.73 (b, 2H, NCH_2 (furfuryl)), 6.12, 6.29 (b, 1H, H–4 (furyl)), 6.35, 6.42 (b, 1H, H–3 (furyl)), 7.32, 7.34 (b, 1H, H–5 (furyl)), 7.46–7.73 (protons of PPh_3). ^{13}C NMR (ppm): $\delta = 25.0$ (C–4), 25.4 (C–3), 29.9 (C–2), 41.5, 41.8 (NCH_2 (furfuryl)), 59.8 (C–1), 110.4, 110.9, 142.2, 147.7 (Aryl−C (furyl)), 128.1–134.2 (Aryl−C (PPh_3)), 205.3 (SCS). ^{31}P NMR (ppm): $\delta = 29.2$. Anal. Calcd. for $C_{31}H_{31}N_2S_3PONi$ (%): C, 58.78; H, 4.93; N, 4.42. Found (%): C, 58.49; H, 4.84, N, 4.34.

Preparation of Complex 4

The same procedure was used as earlier except that complex **2** was used instead of complex **1**.

Yield: 71%. mp 180 °C. IR (KBr, cm^{-1}) 1517 (ν_{C-N}), 1024 (ν_{C-S}), 2091 (NCS), 2926, 2866 ($\nu_{C-H(aliph.)}$), 3074 ($\nu_{C-H(arom.)}$). UV-Vis ($CHCl_3$, λ_{max}/nm (ε/L mol^{-1} cm^{-1})): 487 (604), 331 (45900), 250 (69100). ^{1}H NMR (ppm): $\delta = 2.98$, 3.14 (b, 2H, NCH_2-C$\underline{H}_2-C_4H_3S$), 3.56, 3.73 (b, 2H, NC$\underline{H}_2-CH_2-C_4H_3S$), 4.47, 4.69 (b, 2H, NCH_2 (benzyl)), 6.65–7.78 (Aryl−H). ^{13}C NMR (ppm): $\delta = 27.4$ ($NCH_2-\underline{C}H_2-C_4H_3S$), 50.1 (N$\underline{C}H_2-CH_2-C_4H_3S$), 52.9 ($NCH_2$ (benzyl)), 124.6–139.0 (Aryl−C), 205.7 (SCS). ^{31}P NMR (ppm): $\delta = 20.2$, 29.4. Anal. Calcd. for $C_{33}H_{29}N_2S_4PNi$ (%): C, 61.58; H, 4.55; N, 1.44. Found (%): C, 60.80; H, 4.39; N, 1.40.

Preparation of Complex 5

A mixture of complex **1** (0.56 g, 1.0 mmol), $NiCl_2{\cdot}6H_2O$ (0.237 g, 1.0 mmol), PPh_3 (1.048 g, 4.0 mmol), and $NaClO_4$ (0.242 g, 1.0 mmol) was refluxed for 3 h in

chloroform–methanol solvent mixture (3.2, 50 mL). The purple red solution obtained was filtered and left for evaporation. After 2 days, a purple red solid separated out, which was recrystallized from chloroform.

Yield: 60%. mp 210 °C. IR (KBr, cm^{-1}) 1479 (ν_{C-N}), 1021 (ν_{C-S}), 1088 (ClO_4), 2923, 2852 ($\nu_{C-H(aliph.)}$), 3057 ($\nu_{C-H(arom.)}$). UV-Vis ($CHCl_3$, λ_{max}/nm (ε/L mol^{-1} cm^{-1})): 480 (135), 322 (5920), 239 (33100). ^{1}H NMR (ppm): δ = 1.04–1.12 (m, 1H, H–4 (ax)), 1.46 (q, J = 11.6 Hz, 4H, H–3), 1.69 (bd, 1H, H–4 (eq)), 1.78 (bd, 4H, H–2), 4.08 (b, 1H, H–1), 4.67 (s, 2H, NCH_2 (furfuryl)), 6.11 (b, 1H, H–4 (furyl)), 6.32 (b, 1H, H–3 (furyl)), 7.14–7.76 (protons of PPh_3), 7.33 (b, 1H, H–5 (furyl)). ^{13}C NMR (ppm): δ = 24.8 (C–4), 25.3 (C–3), 29.8 (C–2), 42.2 (NCH_2 (furfuryl)), 60.4 (C–1), 110.9, 111.4, 142.6, 147.2 (Aryl−C (furyl)), 128.6–134.0 (Aryl−C (PPh_3)). ^{31}P NMR (ppm): δ = 29.4, 31.2. Anal. Calcd. for $C_{48}H_{46}S_2P_2O_5NClNi$ (%): C, 61.52; H, 4.95; N, 1.49. Found (%): C, 61.26; H, 4.87; N, 1.47.

Preparation of Complex 6

The same procedure was used as above except that complex **2** was used instead of complex **1**.

Yield: 66%. mp 170 °C. IR (KBr, cm^{-1}) 1502 (ν_{C-N}), 1024 (ν_{C-S}), 1090 (ClO_4), 2921, 2849 ($\nu_{C-H(aliph.)}$), 3055 ($\nu_{C-H(arom.)}$). UV-Vis ($CHCl_3$, λ_{max}/nm (ε/L mol^{-1} cm^{-1})): 485 (206), 324 (22000), 235 (3550). ^{1}H NMR (ppm): δ = 2.99, 3.13 (b, 2H, $NCH_2-C\underline{H}_2-C_4H_3S$), 3.46, 3.72 (b, 2H, $NC\underline{H}_2-CH_2-C_4H_3S$), 4.64 (s, 2H, NCH_2 (benzyl)), 6.70–7.69 (Aryl−H). ^{13}C NMR (ppm): δ = 27.5 ($NCH_2-\underline{C}H_2-C_4H_3S$), 50.2, 50.5 ($N\underline{C}H_2-CH_2-C_4H_3S$), 52.9 ($NCH_2$ (benzyl)), 124.4–139.6 (Aryl−C). ^{31}P NMR (ppm): δ = 29.2, 30.9, 31.4, 43.4. Anal. Calcd. for $C_{50}H_{44}O_4S_3P_2NClNi$ (%): C, 61.58; H, 4.55; N, 1.44. Found (%): C, 60.80; H, 4.39; N, 1.40.

Supplementary Data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 873101. Copies of the data can be obtained, free charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel.: +44 (0) 1223 762911; E-mail: kamila@ccdc.cam.ac.uk).

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