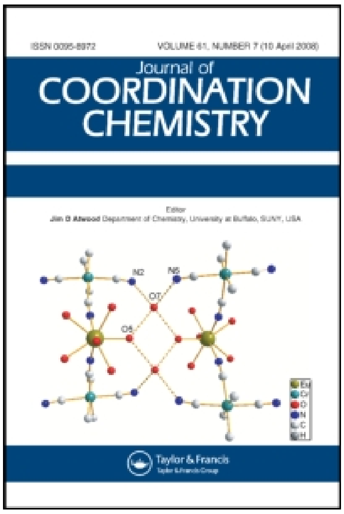

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<i>Trans</i> influences of Cl^-, NCO^- and NCS^- donors on planar $NiS_2PN(CO)$, $NiS_2PN(CS)$, NiS_2PCl and NiS_2P_2 chromophores: synthesis, NMR spectral and single crystal X-ray structural studies

Ramalingam Baskaran[a]; Kuppukkannu Ramalingam[a]; Raghavan Thiruneelakandan[b]; Balasubramaniyam Arul Prakasam[a]; Gabriele Bocelli[c]; Andrea Cantoni[c]
[a] Department of Chemistry, Annamalai University, Annamalainagar, India [b] Department of Chemistry, Anna University, Tiruchirappalli, India [c] IMEM, CNR, Parma, Italy

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Trans influences of Cl^-, NCO^- and NCS^- donors on planar $NiS_2PN(CO)$, $NiS_2PN(CS)$, NiS_2PCl and NiS_2P_2 chromophores: synthesis, NMR spectral and single crystal X-ray structural studies

RAMALINGAM BASKARAN†, KUPPUKKANNU RAMALINGAM*†,
RAGHAVAN THIRUNEELAKANDAN‡, BALASUBRAMANIYAM
ARUL PRAKASAM†, GABRIELE BOCELLI§ and ANDREA CANTONI§

†Department of Chemistry, Annamalai University, Annamalainagar, India
‡Department of Chemistry, Anna University, Tiruchirappalli, India
§IMEM, CNR, Parma, Italy

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Planar [Ni(bedtc)(PPh_3)Cl] (**1**), [Ni(bedtc)(PPh_3)(NCO)] (**2**), [Ni(bedtc)(PPh_3)(NCS)] (**3**), [Ni(bedtc)(PPh_3)(CN)] (**4**) and [Ni(bedtc)(dppe)]ClO_4 (**5**) (where bedtc = *N*-benzyl-*N*-(2-hydroxyethyl)dithiocarbamate anion, PPh_3 = triphenylphosphine and dppe = 1,2-bis((diphenylphosphino)ethane)) were prepared from [Ni(bedtc)$_2$]. Complexes **1**–**5** were characterized by elemental analysis, electronic, IR and NMR (^1H, ^{13}C, and ^{31}P) spectra. Electronic spectra of the complexes show bands corresponding to $dz^2 \rightarrow dxy/dx^2-y^2$ transitions. The complexes were diamagnetic. IR and ^{13}C NMR studies indicate the mesomeric flow of π-electron density from the dithiocarbamate towards the nickel. In ^1H NMR, α-CH_2– and β-CH_2– protons of –CH_2–CH_2–OH were equally deshielded. The deshielding for the coordinated phosphorus signals in ^{31}P NMR spectra for all the cases compared with the free phosphine clearly manifests the drift of electron density from the phosphorus toward the metal on complexation. Single crystal X-ray structures of **1**–**3** indicate that nickel is in a planar environment with short $>S_2C$–N bond distances. In **2**, a rare mode of coordination between nickel and cyanate (NCO^-) through the nitrogen is observed. Significant asymmetry in Ni–S bond distances were observed for **1**–**3** clearly supporting the *trans* influences of Cl^-, NCO^- and NCS^-, respectively, over PPh_3.

Keywords: Nickel; Dithiocarbamate; Triphenylphosphine; dppe; X-ray crystallography; NMR

1. Introduction

Dithiocarbamate (dtc) ligands display a strong propensity of binding to divalent nickel [1–4]. The chemistry of these compounds has been renewed with the utilization of dtc as coadjuvant in AIDS treatment [5, 6]. These compounds have also been proposed for tuberculosis [7] and cancer [8, 9] treatment. The diversity in applications inherent to nickel(II) complexes with simple and chelating phosphines as catalysts [10–12] and in the medicinal field [9], combined with their structural novelty has resulted in synthesis

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*Corresponding author. Email: krauchem@yahoo.com

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of NiS_2PX (X = halogens or N or C or S) chromophores. Group 10 dithiocarbamato complexes with phosphine and nitrogen ligands have been in the limelight because of their structures and biological profiles. Unlike its congeners, Ni(II) is a borderline acceptor and its planar dtc complexes prefers to react with soft Lewis bases such as phosphines over harder nitrogen bases. The symbiotically-induced softness of substituents on the dithiocarbamato ligands was important when determining the reactivity [1, 13, 14]. In our continuing efforts to investigate the synthetic and structural chemistry of dtc's and to understand the influence of Cl^-, CN^-, NCS^- and NCO^- donors on the coordination environment around nickel, we report the synthesis and spectral properties of **1**–**5** along with the single crystal X-ray structures of **1**–**3**.

2. Experimental

All the reagents and solvents employed were commercially available, analytical grade materials, and used as supplied. Electronic spectra of the complexes were recorded on a HITACHI U-2001 spectrophotometer using CH_2Cl_2 as the solvent. IR spectra were recorded on ABB Bomem MB 104 and Avatar Nicolet FT-IR spectrophotometers (range 4000–400 cm^{-1}) as KBr pellets. NMR spectra of the complexes were recorded on a Bruker AMX 400 spectrometer at room temperature using $CDCl_3$ as solvent and TMS as the internal reference. The ^{13}C NMR spectra were recorded in proton decoupled mode.

2.1. *Preparation of the complexes*

2.1.1. Bis(*N*-benzyl-*N*-(2-hydroxyethyl)dithiocarbamato)nickel(II) [Ni(bedtc)$_2$]. A mixture of 20 mmol (2.8 mL) of 2-(benzylamino)ethanol and 20 mmol (1.2 mL) of carbondisulfide in ethanol were kept ice-cold (5°C) to form yellow solution of the dithiocarbamic acid. To this pale yellow dithiocarbamic acid solution, an aqueous solution of $NiCl_2 \cdot 6H_2O$ (2.38 g, 10 mmol) was added with constant stirring. Pale green solid was filtered, washed with water and alcohol, and then dried over anhydrous calcium chloride (Yield: 70%, dec.: 172°C). Anal. Calcd for $C_{20}H_{24}N_2NiO_2S_4$: C, 47.0; H, 4.7; N, 5.5. Found: C, 46.7; H, 4.4; N, 5.2%.

2.1.2. (*N*-benzyl-*N*-(2-hydroxyethyl)dithiocarbamato)chloro(triphenylphosphine) nickel(II) [Ni(bedtc)(PPh$_3$)Cl] (1). A mixture of [Ni(bedtc)$_2$] (256 mg, 0.5 mmol), PPh_3 (262 mg, 1 mmol) and $NiCl_2 \cdot 6H_2O$ (119 mg, 0.5 mmol) was refluxed for 3 h in methanol : acetonitrile (1 : 1, 50 mL) and then concentrated to ca. 25 mL. The resultant dark purple-red solution was filtered and left for evaporation. After 3 days, fine single crystals suitable for X-ray structural analysis were obtained (Yield: 70%, dec.: 149°C). Anal. Calcd for $C_{28}H_{27}ClNNiOPS_2$: C, 57.7; H, 4.7; N, 2.4. Found: C, 57.5; H, 4.3; N, 2.1% (figure 1).

2.1.3. (*N*-benzyl-*N*-(2-hydroxyethyl)dithiocarbamato)(cyanato-N)(triphenylphosphine) nickel(II) [Ni(bedtc)(PPh$_3$)(NCO)] (2). A mixture of [Ni(bedtc)$_2$] (256 mg, 0.5 mmol), PPh_3 (262 mg, 1 mmol), $NiCl_2 \cdot 6H_2O$ (119 mg, 0.5 mmol) and KCNO (81 mg, 1 mmol) was refluxed for 3 h in methanol : acetonitrile (1 : 2, 60 mL), concentrated to ca. 30 mL and filtered through filter paper. The purple-red filtrate on slow evaporation gave a purple-red solid. Single crystals suitable for X-ray structural analysis were obtained by recrystallization from acetonitrile (Yield: 60%, dec.: 170°C). Anal. Calcd for $C_{29}H_{27}N_2NiO_2PS_2$: C, 59.1; H, 4.6; N, 4.8. Found: C, 58.7; H, 4.3; N, 4.5% (figure 2).

2.1.4. (*N*-benzyl-*N*-(2-hydroxyethyl)dithiocarbamato)(thiocyanato-N)(triphenylphosphine)-nickel(II) [Ni(bedtc)(PPh$_3$)(NCS)] (3). A mixture of [Ni(bedtc)$_2$] (256 mg, 0.5 mmol), PPh$_3$ (262 mg, 1 mmol), $NiCl_2 \cdot 6H_2O$ (119 mg, 0.5 mmol) and NH_4SCN (76 mg, 1 mmol) in methanol–acetonitrile (1 : 2, 60 mL) was refluxed for 2 h, concentrated to ca. 30 mL, the purple-red solution filtered and allowed to stand for 2 days. The purple-

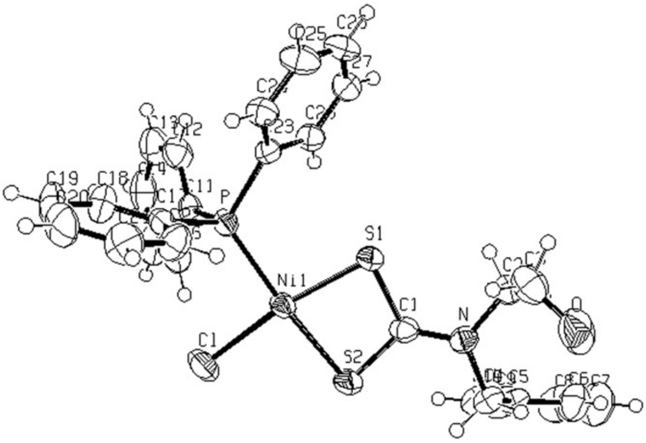

Figure 1. Thermal ellipsoid plot of [Ni(bedtc)(PPh$_3$)Cl].

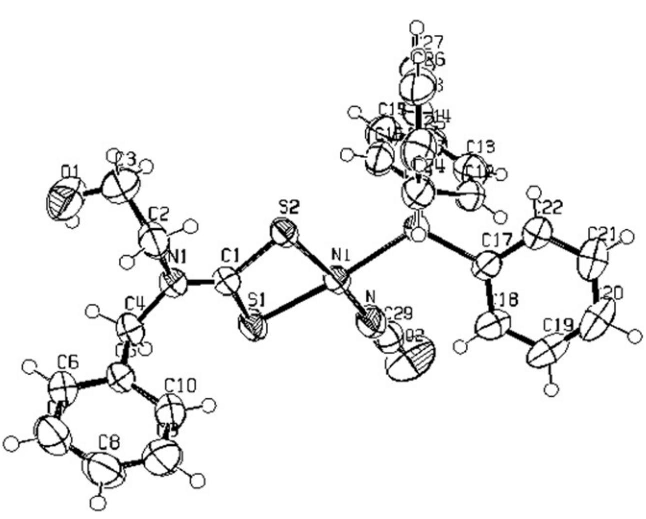

Figure 2. Thermal ellipsoid plot of [Ni(bedtc)(PPh$_3$)(NCO)].

red solid was filtered and dried over anhydrous calcium chloride. Single crystals suitable for X-ray structural analysis were obtained by recrystallization from the same solvent mixture (Yield: 75%, dec.: 189°C). Anal. Calcd for $C_{29}H_{27}N_2NiOPS_3$: C, 57.5; H, 4.5; N, 4.6. Found: C, 57.2; H, 4.2; N, 4.3% (figure 3).

2.1.5. (*N*-benzyl-*N*-(2-hydroxyethyl)dithiocarbamato)(cyano-C)(triphenylphosphine)-nickel(II) [Ni(bedtc)(PPh$_3$)(CN)] (4). A mixture of [Ni(bedtc)$_2$] (256 mg, 0.5 mmol), PPh_3 (262 mg, 1 mmol), $NiCl_2 \cdot 6H_2O$ (119 mg, 0.5 mmol) and KCN (65 mg, 1 mmol) was refluxed for 3 h in methanol : acetonitrile (2 : 1, 60 mL), then concentrated to ca. 30 mL and the orange-yellow solution obtained was filtered and left for evaporation. The solid separated was filtered and dried over anhydrous calcium chloride (Yield: 65%, dec.: 175°C). Anal. Calcd for $C_{29}H_{27}N_2NiOPS_2$: C, 60.8; H, 4.7; N, 4.9. Found: C, 60.5; H, 4.4; N, 4.5%.

2.1.6. (*N*-benzyl-*N*-(2-hydroxyethyl)dithiocarbamato)(1,2-bis(diphenylphosphino)ethane)-nickel(II) perchlorate [Ni(bedtc)(dppe)]ClO$_4$ (5). A mixture of [Ni(bedtc)$_2$] (256 mg, 0.5 mmol), dppe (398 mg, 1 mmol), $NiCl_2 \cdot 6H_2O$ (119 mg, 0.5 mmol) and NH_4ClO_4 (117 mg, 1 mmol) was refluxed in dichloromethane–methanol (1 : 1, 50 mL) for 3 h, followed by concentration to ca. 25 mL. The solution was filtered and left for evaporation. After 2 days, an orange-red solid was filtered and dried over anhydrous calcium chloride (Yield: 70%, dec.: 183°C). Anal. Calcd for $C_{36}H_{36}ClNNiO_5P_2S_2$: C, 55.2; H, 4.6; N, 1.8. Found: C, 54.8; H, 4.4; N, 1.4%.

2.2. *X-ray crystallography*

Details of crystal data, data collection and refinement parameters for **1**–**3** are summarized in table 1. The intensity data were collected at ambient temperature (293 K) on a Philips PW1100 diffractometer [15] using graphite monochromated Mo-Kα radiation for **1** ($\lambda = 0.71073$ Å) and **3** ($\lambda = 0.71069$ Å). The intensity data for **2** were collected at 293 K on a Siemens AED diffractometer using Cu-Kα radiation

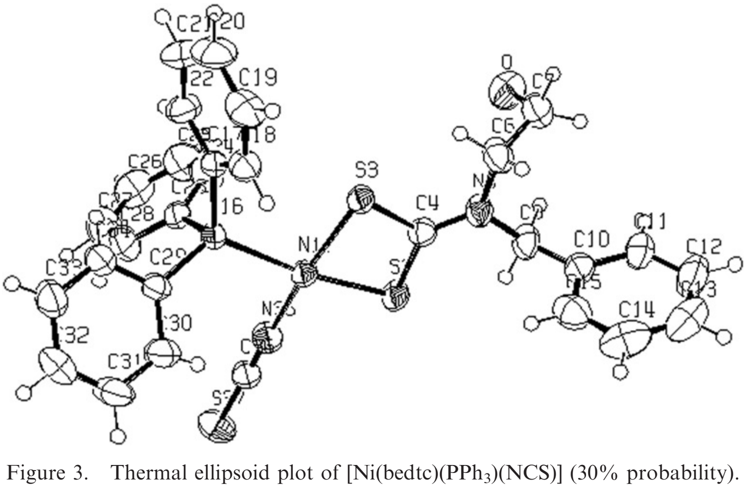

Figure 3. Thermal ellipsoid plot of [Ni(bedtc)(PPh$_3$)(NCS)] (30% probability).

($\lambda = 1.54178$ Å). For **1–3**, structures were solved by SHELXS-97 [16] and refined by SHELXL-97 [17]. Absorption corrections were performed by two methods. North *et al.*'s [18] method was employed for **1** and **3**, and for **2** Walker and Stuart's [19] method with a program written by Gluzinski [20] was used. For **1** and **2**, experimentally deduced unit cells were used. All non-hydrogen atoms were refined anisotropically and the hydrogen atom positions were fixed using geometrical constraints. Molecular plots were obtained with ORTEP [21]. Selected bond distances and angles of **1–3** are summarized in table 2.

3. Results and discussion

3.1. *Electronic spectra*

Electronic spectra show bands at 513, 495, 483, 435, and 435 nm for complexes **1–5**, respectively, due to d–d transitions. For the parent [Ni(bedtc)$_2$] the d–d transition bands

Table 1. Crystal data, data collection and refinement parameters for **1–3**.

Complex	**1**	**2**	**3**
Chemical formula	$C_{14}H_{13.5}Cl_{0.5}N_{0.5}Ni_{0.5}O_{0.5}P_{0.5}S$	$C_{29}H_{27}N_2NiO_2PS_2$	$C_{29}H_{25}N_2NiOPS_3$
FW	291.4	589.3	603.4
Crystal dimensions (mm)	0.13 × 0.15 × 0.23	0.15 × 0.17 × 0.26	0.14 × 0.17 × 0.18
Crystal system	Monoclinic	Triclinic	Triclinic
Color	Purple	Pale reddish brown	Purple
Habit	Prism	Triangular–based prism	Prism
Space group	$P\ 2_1$	$P\ -1$	$P\ -1$
a (Å)	9.198(2)	10.64(2)	11.172(3)
b (Å)	14.563(3)	13.81(2)	14.647(2)
c (Å)	10.770(2)	10.23(2)	10.059(2)
α (°)	90	96.65(2)	107.430(3)
β (°)	107.98(2)	106.83(2)	108.090(3)
γ (°)	90	74.33(2)	72.020(2)
U (Å^3)	1372.2(5)	1384 (4)	1450.0(5)
Z	4	2	2
D_c (g cm^{-3})	1.410	1.414	1.382
μ (cm^{-1})	1.037	3.202	0.965
$F(000)$	604	612	624
λ (Å)	Mo-Kα (0.71073)	Cu-Kα (1.54178)	Mo-K (0.71069)
θ Range (°)	3.43–29.99	3.33−69.92	3.00–30.02
Scan type	$\omega{-}2\theta$	$\backslash\theta/2\backslash\theta$	$\omega - 2\theta$
Index ranges	$-12<h<12$; $0<k<20$; $0<l<15$	$-12<h<2$; $-16<k<16$; $-12<l<12$	$-15<h<14$; $-20\le k\le 19$; $0\le l\le 14$
Reflections collected	4135	5241	8477
Observed reflections $F_o > 2\sigma\ (F_O)$	2770	3631	5777
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 0.0000P]$ $P = \max\ (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1311P)^2 + 0.0000P]$ $P = \max\ (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 0.0000P]$ $P = \max(F_o^2 + 2F_c^2)/3$
Number of parameters refined	316	334	338
Final R, Rw (observed, data)	0.0392; 0.0656	0.0583; 0.1801	0.0402; 0.1052
Goodness-of-fit	0.915	1.023	0.961

Table 2. Selected bond distances and angles for **1**–**3**.

1		**2**		**3**	
Bond distances					
Ni(1)–S(1)	2.1854(12)	Ni–N	1.892(5)	Ni(1)–N(35)	1.8669(18)
Ni(1)–Cl	2.1858(12)	Ni–S(2)	2.177(3)	Ni(1)–S(3)	2.1726(6)
Ni(1)–P	2.2091(11)	Ni–P	2.193(3)	Ni(1)–P(16)	2.2037(6)
Ni(1)–S(2)	2.2177(12)	Ni–S(1)	2.219(3)	Ni(1)–S(2)	2.2157(6)
S(1)–C(1)	1.735(4)	S(1)–C(1)	1.719(5)	S(2)–C(4)	1.7257(19)
S(2)–C(1)	1.701(4)	S(2)–C(1)	1.740(5)	S(3)–C(4)	1.7306(19)
N–C(1)	1.324(5)	C(29)–N	1.043(6)	C(4)–N(5)	1.302(2)
N–C(2)	1.475(5)	N(1)–C(1)	1.286(5)	N(35)–C(36)	1.141(3)
N–C(4)	1.476(4)	C(29)–O(2)	1.247(7)	C(36)– S(37)	1.625(2)
Bond angles					
S(1)–Ni(1)–P	96.46(4)	N–Ni–P	91.07(19)	N(35)–Ni(1)–P(16)	92.11(6)
Cl–Ni(1)–P	92.20(5)	S(2)–Ni–P	96.06(15)	S(3)–Ni(1)–P(16)	95.75(2)
S(1)–Ni(1)–S(2)	78.45(4)	N–Ni–S(1)	93.97(19)	N(35)–Ni(1)–S(2)	93.07(6)
Cl–Ni(1)–S(2)	93.44(5)	S(2)–Ni–S(1)	78.82(14)	S(3)–Ni(1)–S(2)	78.89(2)
C(23)–P–Ni(1)	113.42(12)	C(2)–N(1)–C(4)	116.6(4)	N(5)–C(4)–S(2)	126.52(15)
N–C(1)–S(2)	127.3(3)	C(29)–N–Ni	170.9(5)	N(5)–C(4)–S(3)	125.93(15)
N–C(1)–S(1)	124.4(3)	N(1)–C(1)–S(1)	126.4(3)	S(2)–C(4)–S(3)	107.54(11)
C(1)–N–C(2)	121.2(3)	N(1)–C(1)–S(2)	126.0(3)	C(36)–N(35)–Ni(1)	176.2(2)
S(2)–C(1)–S(1)	108.3(2)	S(1)–C(1)–S(2)	107.6(3)	N(35)–C(36)–S(37)	178.7(2)

were observed at 480 and 632 nm. Based on single crystal electronic spectral studies of similar complexes, the band in the region 435–513 nm for **1**–**5** and the parent [Ni(bedtc)$_2$] is attributed to the $dz^2 \rightarrow dx^2 - y^2$ transition [22] and the band at 632 nm for [Ni(bedtc)$_2$] is due to $dxy \rightarrow dx^2 - y^2$. For **4** and **5**, $\lambda_{\max}$ is observed at 435 nm, which is very low and is attributed to greater ligand field stabilization energy exerted by cyanide ion and the chelating phosphine (dppe exerts a strong crystal field close to that of cyanide). In all the complexes, the charge-transfer bands were observed below 400 nm [22]. Electronic spectral data of the complexes support the square-planar geometry around the nickel atom.

3.2. *IR spectral studies*

IR spectra show $\nu_{(C\text{–}N)}$ bands at 1514, 1515, 1517, 1520, and 1517 cm^{-1} for **1**–**5**, respectively. The shift in $\nu_{(C\text{–}N)}$ values to higher wave number compared with parent [Ni(bedtc)$_2$] complex observed at 1497 cm^{-1} is due to the mesomeric drift of electron density from the dtc ligand towards nickel, increasing the contribution of polar thioureide. The bands at 2253 (for **2**), 2085 (for **3**) and 2119 cm^{-1} (for **4**) indicates the presence of N-coordinated NCO$^-$, N-coordinated NCS$^-$ and C-coordinated cyanide, respectively [14]. The $\nu_{(C\text{–}S)}$ appeared at 991–997 cm^{-1} without splitting, supporting the bidentate coordination of dtc in all cases.

3.3. *NMR spectral studies*

The ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts of the synthesized complexes are summarized in table 3.

Table 3. NMR chemical shifts of the complexes (in ppm).

Compound	NMR	α-CH_2–[a]	β-CH_2–	Benzyl –CH_2–	–OH	PPh_x[b]	N $^{13}CS_2$ (Thioureide)	–CH_2–(dppe)
(**1**)	^1H	3.55–3.85		4.83–4.95	2.16	7.14–7.84	–	–
	^{13}C	50.3	60.2	53.4	–	128.4–134.5	206.6	–
	^{31}P	–	–	–	–	19.9	–	–
(**2**)	^1H	3.48–3.87		4.76–4.96	2.17	7.15–7.82	–	–
	^{13}C	50.0	60.1	53.5		128.5–134.1[c]	205.7	–
	^{31}P			–	–	20.7	–	–
(**3**)	^1H	3.48–3.84		4.76–4.94	2.18	7.33–7.73	–	–
	^{13}C	50.5	59.8	53.6	–	128.9–134.1[c]	205.1	–
	^{31}P	–	–	–	–	21.7	–	–
(**4**)[d]	^1H	3.68–3.87		4.92–4.99	2.19	7.26–7.68	–	–
	^{13}C				–			–
	^{31}P	–	–	–	–		–	–
(**5**)	^1H	3.71–3.91		5.00–5.20	2.61	7.30–7.76	–	1.72
	^{13}C	50.8	59.7	53.9	–	126.9–133.4	202.7	26.2
	^{31}P	–	–	–	–	61.1	–	–
[Ni(bedtc)$_2$]	^1H	3.68–3.86		4.96	2.19	7.26–7.40		–

Notes: [a]α-CH_2– and β-CH_2– proton signals in ^1H NMR appear as a broad singlet because of substantial barrier to C–N bond rotation.

[b]Signals from phenyl ring of benzyl group (^1H and ^{13}C) also merged with the PPh_x signals; $x = 3$ for (**1**)–(**3**).

[c]In complexes (**2**) and (**3**) the NCO^- and NCS^- chemical shifts merged with those of the aromatic carbon signals.

[d]^{13}C NMR of (**4**) has not been recorded due to its very limited solubility in common deuterated solvents.

3.3.1. ^{1}H NMR.

In all the complexes, α-CH_2– and β-CH_2– protons of –CH_2–CH_2–OH and benzylic –CH_2– protons appear as two broad signals due to the asymmetry in the coordination environment, indicating a substantial barrier to C–N bond rotation. In table 3, only the regions are given for proton signals and no individual splitting assignments are made. The α-methylene protons of –CH_2–CH_2–OH are adjacent to nitrogen of thioureide π system and similarly β-methylene protons of –CH_2–CH_2–OH are adjacent to oxygen. Hence, the α and β protons experience strong deshielding and appear as broad singlets in the region 3.48–3.91 ppm. The benzylic –CH_2– protons give rise to a signal in the downfield region of 4.76–5.20 ppm. Aromatic protons of phenyl ring resonate in the region 7.14–7.87 ppm and the –OH protons appear as a singlet around 2.16–2.61 ppm for **1**–**5**, as expected. The methylene protons of chelating dppe in **5** appear at 1.72 ppm.

3.3.2. ^{13}C NMR.

For the mixed ligand complexes **1**, **2**, **3**, and **5**, the signals in the downfield region (202.7–206.6 ppm) with low intensity are of thioureide ($N^{13}CS_2$). The same thioureide carbon signal of [Ni(bedtc)$_2$] appears at 207 ppm. The slight upfield shift for **1**, **2**, **3**, and **5** from normal chemical shift values of [Ni(dtc)$_2$] (206–210 ppm) [23] is due to mesomeric shift of electron density from dtc toward the metal center. The observation is in line with the observation from higher $\nu_{(C-N)}$ in their IR spectra.

From ^{13}C NMR spectra of the complexes, the chemical shifts of the carbon of thioureide $N^{13}CS_2$ are correlated to the π-bonding in the $>NCS_2$ fragment. Generally, higher $\nu_{(C-N)}$ values correlate with lower $>N^{13}CS_2$ chemical shifts for d-block elements and vice-versa for main group metals [23]. The alleviation of excess electron density on nickel by PPh_3, cyanate, isothiocyanate and dppe results in a drift of electron density toward the metal through the thioureide bond and hence significant upfield shifts are observed. The $>N^{13}CS_2$ signal for **5** is significantly more shielded (202.7 ppm) than for neutral complexes **1**–**3** from the back bonding ability of dppe. In **2** and **3**, the NCO^- and NCS^- chemical shifts appear to merge with those of the aromatic carbon signals. For **1**, **2**, **3**, and **5**, the benzylic $–CH_2–$ carbon shows a signal in the range 53.4–53.9 ppm. In $–CH_2–CH_2–OH$ group, β-CH_2– carbons are deshielded by oxygen and observed in the range 59.7–60.2 ppm. The signal around 50.0–50.8 ppm is assigned to α-CH_2– carbons.

3.3.3. ^{31}P NMR. Triphenylphosphine shows a signal at −5 ppm [24] and a coordinated phosphine shows a signal around 20 ppm. Similarly, free dppe shows a signal at −13 ppm [24] and coordinated dppe shows a signal around 60 ppm. Complex **5** with chelating dppe gives a signal at 61.1 ppm. The ^{31}P signals for **1**, **2**, **3**, and **4** appear at 19.9, 20.7, 21.7, and 28.9 ppm, respectively. Deshielding of the coordinated phosphorus is the largest for cyano complex **4** [28.9 ppm], attributed to higher back bonding ability of cyanide ion, also shown by higher $\nu_{(C–N)}$.

3.4. *Structural analysis*

The single crystal X–ray structure of **1** contains discrete mononuclear [Ni(bedtc)(PPh_3)Cl] units with insignificant intermolecular association. Four formula units are present in the unit cell. Ni(1), S(1), S(2), P, and Cl are coplanar, consistent with the observed diamagnetism of the complex. The molecule is not of ideal square-planar geometry because of the small bite angle [78.45(4)°] associated with the dtc ligand. The two Ni–S bond distances, 2.1854(12) Å and 2.2177(12) Å, are different due to different *trans* influences exerted by phosphine and Cl^-. PPh_3 exerts a better *trans* influence and hence the Ni–S bond *trans* to phosphorus is longer than that *trans* to Cl^-. The short thioureide [C(1)–N] distance observed, 1.324(5) Å, indicates that π-electron density is delocalized over S_2CN moiety and that this bond has a double bond character. This is also confirmed by the two S–C–N angles [124.4(3)° and 127.3(3)°] being greater than the S–C–S angle, 108.3 (2)°. The contribution of the thioureide form to the dtc, indicated by relatively short C–N bond length, contrasts with the adjacent single bond N–C distances.

The C–S bond lengths, 1.735(4) Å and 1.701(4) Å, are shorter than C–S single bond length of 1.81 Å and longer than C=S distance of 1.69 Å, indicating partial double bond character. The Ni–P and Ni–Cl distances in **1** are 2.2091(11) Å and 2.1858(12) Å, respectively. The Ni–P distance is relatively short compared to a long Ni–P (2.40 Å) distance reported in the literature [25]. The P–Ni–Cl angle is 92.20(5)°; phenyl rings show normal bond parameters.

[Ni(bedtc)(PPh_3)(NCO)] (**2**) is monomeric with insignificant intermolecular contacts. Two formula units are present in the unit cell. Planarity around nickel is supported by the diamagnetic nature of the complex. Due to the difference in the *trans* influence of phosphine and NCO^- the two Ni–S bond distances [2.177(3) Å and 2.219(3) Å] are slightly different. The thioureide distance [C(1)–N(1) = 1.286(5) Å] is very short, indicating extensive delocalization of π-electrons over S_2CN moiety. Thioureide bond distances are shorter for the mixed ligand complexes in general. Among the three mixed ligand complexes, **2** shows very short thioureide distance due to the π-acidic nature of the triphenylphosphine and cyanate groups. This is also confirmed by the fact that the two S–C–N angles [126.0(3)° and 126.4(3)°] are much greater than that of S–C–S, 107.6 (3)°.

The Ni–P distance [2.193(3) Å] is very short. The Ni–N distance in Ni–NCO, 1.892(5) Å, is also short, showing effective bonding between nickel and cyanate ion. Nitrogen of NCO^- is coordinated to Ni, which is a rare mode of coordination. The N–C bond length [1.043(6) Å] of NCO^- indicates the presence of a double bond and C–O distance of 1.247(7) Å is also very short. The P–Ni–N angle is 91.07(19)° and the Ni–N–C(29) angle is 170.9(5)°, significantly bent to accommodate PPh_3. The reduction in angle allows the bulky PPh_3 to form a strong bond. The N–C–O bond angle, 176.2(6)°, deviates from linearity, also due to steric repulsions of the bulky PPh_3.

In the single crystal X-ray structure of **3**, two mononuclear [Ni(bedtc)(PPh_3)(NCS)] units are present in the unit cell with no significant intermolecular contacts. Planarity of the coordination around Ni(II) manifests itself in the observed diamagnetism of the compound.

In **3**, the two Ni–S bond distances [2.1726(6) Å and 2.2157(6) Å] are highly asymmetric because of the different *trans* influences exerted by PPh_3 and NCS^-. The asymmetry in Ni–S bond distances leads to a change in Ni–S–C and S–C–S angles. The C–N (thioureide) bond is short, 1.302(2) Å in **3**, symbolizing the mesomeric flow of π-electron density from nitrogen to metal center through carbon. Hence, C–N is of double bond character, consistent with two S–C–N angles [126.52(15)° and 125.93(15)°] being much greater than the S–C–S angle [107.54(11)°].

The C–S bond distances 1.7257(19) Å and 1.7306(19) Å, intermediate between single and double bond distances, exemplify the partial double bond character. The other bond parameters of the phenyl rings are normal. The C–P–C angles deviate appreciably from tetrahedral and crowding of the phenyl rings causes the P–C–C angles to be asymmetric. The Ni–N distance, 1.8699(18) Å, is considerably shorter than the distance cited for [Ni(en)$_2$(NCS)$_2$], 2.15 Å, which shows the effective bonding between nickel and NCS^-. The P–Ni–N angle 92.11(6)° supports the planarity of the molecule. The Ni–N–C angle 176.2(2)° is almost linear. However, N(35)–C(36)–S(37) angle is 178.7(2)° for linear isothiocyanate. The short C–N and C–S bond distances in NCS^-, 1.141(3) Å and 1.625(2) Å respectively, indicate the double bonds.

The following points are drawn by comparing the bond parameters of **1**–**3**. All three are distorted square-planar geometry and diamagnetic. Thioureide bond distances are short in all the mixed ligand complexes, supporting a contribution of thioureide form to the complexes. Compound **2** shows the shorter thioureide distance 1.286(5) Å, compared to others, due to π-acidic nature of the PPh_3 and cyanate groups. Dithiocarbamate bite angles (S–Ni–S) in all the complexes are small and almost the same. The observed small bite angle is attributed to the very high steric effect caused by triphenylphosphine ligands and the chelating effect of the dtc group. The Ni–S distances in all three complexes vary in accordance with the variation of *trans* influences of PPh_3, cyanate, thiocyanate and chloride. *Trans* influence of PPh_3 on Ni–S is stronger than those of NCS^-, NCO^-, and Cl^-. Ni–P distances are short in all the complexes, perhaps resulting from strong back bonding from nickel. P–Ni–Cl/N angles are around 92°, which supports the planar coordination around the nickel atom. In all three complexes, C–S bond lengths are asymmetrical and the distances indicate their partial double bond nature. The S–C–S angles are small (around 108°), indicating partial double bonded nature of thioureide (C–N) bond and C–S bond in S_2CN. The ligand having a greater *trans* influencing property (PPh_3) is always bonded to the metal ion (Ni^{2+}) *trans* to the C–S bond having greater partial double bond character in the dtc group and vice versa.

4. Supplementary material

CCDC 280741, 602533, and 629133 contain the supplementary crystallographic data for **1–3**. 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 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk.

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