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Trans influence of triphenylphosphines and pseudohalogens on Ni-S bonds: Synthesis, spectral and single crystal X-ray structural studies on NiS_2PN and NiS_2PC chromophores

Research Article

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Abstract: *Trans* influence of triphenylphosphines and pseudohalogens on Ni-S bonds of NiS_2PN and NiS_2PC chromophores has been investigated by synthesizing and characterizing them. The complexes show the characteristic thioureide IR band at ~ 1530 cm^{-1}. Electronic spectrum of the cyanide analogue shows a strong blue shift relative to others. X-ray structures of [Ni(pipdtc)(4-MP)(NCS)] (**1**), [Ni(pipdtc)(PPh_3)(NCS)] (**2**) and [Ni(pipdtc)(PPh_3)(CN)] (**3**) (pipdtc = piperidinecarbodithioate anion, 4-MP = tri(4-methylphenyl) phopshine) are reported. Ni—S bond distance trans to 4-MP(**1**) is longer than the distances in (**2**) and (**3**) and Ni—S bond distances trans to Ni—NCS/CN decrease as follows: (**3**) > (**2**) > (**1**). Particularly, 4-MP shows a highly significant trans influence than triphenylphosphine on Ni-S bond. Similarly, CN^- exerts a marginally significant trans influence compared to NCS^-. Thioureide C—N distances are relatively very short due to the drift of electron density towards the metal. The Ni—N—C angle (163.5(2)°) observed in (**2**) indicates deviation from linearity to a larger extent compared to that in (**1**) (176.3(3)°) due to the steric effect of the 4-methyl group. The reduction potentials (CV) for the mixed ligand complexes are much less compared to that of the parent NiS_4 chromophore due to the ϖ-acidic phosphines.

Keywords: *Nickel(II) • Trans influence • Cyanide • Thioureide • X-ray crystal structure.*

1. Introduction

Coordination complexes involving group X metal ions, dithiocarbamates, phosphines and different nitrogenous bases exhibit interesting structural variations [1]. Some of the dithiocarabamates find applications in the field of medicine [2]. Divalent nickel is a 'borderline acid' which softens on coordination with soft sulphur atoms of the dithiocarbamate facilitating its reaction with soft donors [3,4]. Bis(dithiocabamato) nickel(II) complexes are planar, diamagnetic and invariably show asymmetry in Ni-S bonds due to variations in the nature of the substituents [5,6]. NiS_4 chromophore of the dithiocarbamates react with substituted phosphines with ease to form [Ni(dtc) PR_3X] complexes. A number of complexes of the general formula, [Ni(dtc)PR_3X] 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 synthesized and structurally characterized from our laboratory [7-10]. Paticularly, electronic spectra of the [Ni(dtc)(PPh_3)X] are highly sensitive to the nature of 'X' ligand and single crystal X-ray structures of (dtc

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= ethylcyclohexyldithiocarbamate) indicate that the planar environment of the complexes is amenable to tetrahedral distortions due to steric influence [11]. Reports on *trans* influences on the distortions in planar $[Ni(dtc)(PPh_3)X]$ chromophores is limited and in continuation of our interest [12,13] in understanding the factors controlling the structure of $[Ni(dtc)(PPh_3)X]$ chromophores, herein we report the synthesis, spectral and structural characterization of [Ni(pipdtc)(4-MP)(NCS)] (**1**), $[Ni(pipdtc)(PPh_3)(NCS)]$(**2**) and $[Ni(pipdtc)(PPh_3)(CN)]$(**3**) (where pipdtc = piperidinedithiocarbamate; 4-MP = tri(4-methylphenyl)phosphine).

2. Experimental procedure

All the reagents and solvents employed were commercially available high-grade purity materials (E-Merck) used as supplied without further purification. IR spectra were recorded on Avator Nicolet FT-IR spectrometer (range: 4000 – 400 cm^{-1}) as KBr pellets. The UV-Visible spectra in CH_2Cl_2 were recorded in a Hitachi U-2001 double beam spectrophotometer.

2.1. Preparation

2.1.1. [Ni(pipdtc)(4-MP)(NCS)] (1)

The parent complex, $[Ni(pipdtc)_2]$ was prepared [14] and was recrystallized from ethanol. A mixture of $[Ni(pipdtc)_2]$ (380 mg, 1 mmol), 4-MP (610 mg, 2 mmol), $NiCl_2•6H_2O$ (240 mg, 1 mmol) and NH_4SCN (150 mg, 2 mmol) in acetonitrile - methanol (1:1, 50 mL) was refluxed for about 3 hours, followed by concentration to ca. 25 mL. The precipitated purple red compound was filtered and was dried over anhydrous calcium chloride. Single crystals suitable for X-ray analysis were obtained by recrystallization from acetonitrile. Yield: 70%; m.p.: 147°C (dec.). For $C_{28}H_{31}N_2NiPS_3$ (581.4) calcd.: 57.83% C, 5.38% H, and 4.82% N; found: 57.80% C, 5.80% H, 4.79% N.

2.1.2. [Ni(pipdtc)(PPh$_3$)(NCS)] (2)

A mixture of $Ni(pipdtc)_2$ (380 mg, 1 mmol), PPh_3 (520 mg, 2 mmol), $NiCl_2•6H_2O$ (240 mg, 1 mmol) and NH_4SCN (150 mg, 2 mmol) in acetonitrile - methanol (1:1, 50 mL) was refluxed for about 3 hours, followed by concentration to ca. 25 mL and was left undisturbed for two days. The precipitated purple red compound was filtered and dried over anhydrous calcium chloride. Single crystals suitable for X-ray analysis were obtained by recrystallization from acetonitrile. Yield: 70%; m.p.: 152°C (dec.). For $C_{25}H_{25}N_2NiPS_3$ (539.3) calcd.: 55.66% C, 4.68% H, 5.19% N; found: 55.63% C, 4.64% H, 5.17% N.

2.1.3. [Ni(pipdtc)(PPh$_3$)(CN)] (3)

A mixture of $[Ni(pipdtc)_2]$ (380 mg, 1 mmol), PPh_3 (520 mg, 2 mmol), $NiCl_2•6H_2O$ (240 mg, 1 mmol) and KCN (130 mg, 2 mmol) in methanol-acetonitrile (2:1, 50 mL) was refluxed for 3 hours, followed by concentration to ca. 25 mL and was then left undisturbed for two days. The precipitated orange yellow compound was filtered and dried over anhydrous calcium chloride. Single crystals suitable for X-ray analysis were obtained by recrystallization from CH_3OH-CH_3CN solvent mixture. Crystals obtained were unstable at room temperature and hence they were kept under liquid paraffin. Yield: 55%; m.p.: 149°C (dec.). Analytical data (for solvent free complex) $C_{25}H_{25}N_2NiPS_2$ (507.3) calcd.: 59.18% C, 5.00% H, 5.52% N; found: 59.14% C, 4.96% H, 4.96% N.

2.2. Cyclic voltammetry

ECDA-001 Basic Electrochemistry system was used for all measurements. Glassy carbon was used as working electrode and the counter electrode was a platinum wire. Electrochemical grade CH_2Cl_2 was used as the solvent. The reference electrode was Ag/AgCl. Tetrabutylammonium perchlorate (0.01 M) was used as the supporting electrolyte. The experiments were carried out in an oxygen free atmosphere by bubbling purified nitrogen gas through the solution at room temperature. The peak potentials showed a maximum variation of +/- 5 mV.

2.3. X-ray crystallography

Details of crystal data, data collection and refinement parameters for the compounds are given in Table 1 and selected bond parameters are listed in Table 2. Intensity data were collected at ambient temperature (293 K) on Bruker AXS smart single crystal diffractometer with CCD (area detector) by using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). The structure was solved by direct method inserted in SHELXTL-NT V5.1 in the Bruker AXS software [15] and the molecular diagrams were drawn with ORTEP – 3 program [16].

3. Results and discussion

3.1. IR and electronic spectra

IR spectra of complexes (**1**), (**2**) and (**3**) show thioureide ν(C-N) bands at 1532, 1531 and 1533 cm^{-1} . The parent bisdithiocarbamate, $[Ni(pipdtc)_2]$ shows the thioureide band at 1508 cm^{-1} [14]. The shift in $\nu_{C\text{-}N}$ value to higher wave number compared to the parent dithiocarbamate is due to increased mesomeric drift of electron density from the dithiocarbamate moiety towards the metal atom. The ν(C-S) bands appear at 1017, 1013 and 1009 cm^{-1} for complexes (**1**), (**2**) and (**3**) respectively without any splitting [17]. The ν(N-C(-S)) band appears at 2090 and 2089 cm^{-1} for (**1**) and (**2**) respectively. The ν(C-N) band for the cyanide appears at 2116 cm^{-1} for compound (**3**). Electronic spectra of (**1**) and (**2**) show bands at ~400 nm due to charge transfer with large optical densities. Another band observed at 478 nm

Table 1. Crystal data, data collection and refinement parameters of (**1**), (**2**) and (**3**).

Complex	(1)	(2)	(3)
Empirical formula	$C_{28}H_{31}N_2Ni\ PS_3$	$C_{25}H_{25}N_2Ni\ PS_3$	$C_{27}H_{25}N_3Ni\ PS_2$
FW	581.4	539.3	545.3
Crystal dimensions/mm	0.19×0.29×0.33	0.19×0.27×0.33	0.14×0.19×0.31
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	12.338(3)	10.483(3)	9.389(2)
b/Å	15.754(4)	13.334(2)	15.494 (3)
c/Å	15.761(3)	10.379(3)	9.240(3)
α/°	96.55(4)	105.56(3)	92.53(3)
β/°	101.17(2)	112.18(2)	97.60(3)
γ/°	99.56(3)	73.26(3)	84.35 (2)
$V/Å^3$	2929.7	1265.5	1325.2
Z	4	2	2
$Dc/g\ cm^{-3}$	1.318	1.415	1.367
μ/cm^{-1}	9.50	10.93	9.70
λ/Å	Mo-Kα (0.71069)	Mo-Kα (0.71069)	Mo-Kα (0.71069)
Θ range/°	3 – 28	3-30	3-30
Scan type	-2θ	-2θ	-2θ
Reflections collected	12750	6866	7715
Observed reflections [Fo > 4σ (Fo)]	7165	4442	4950
Number of parameters refined	820	390	295
Final R, Rw (obs. data)	0.0364, 0.0871	0.0320, 0.0623	0.0442, 0.1092
GOOF	1.007	1.010	0.993

(λmax : 20.920 cm^{-1}, ε: 62450 $mol^{-1}cm^{-1}$) and 482 nm (λmax : 20.747 cm^{-1}, ε : 65410 $mol^{-1}cm^{-1}$) for (**1**) and (**2**) respectively are due to d-d transitions corresponding to dz^2---> dx^2—y^2 transitions and the other transitions in the longer wavelength region are not prominent [7,11]. In complex (**3**), in addition to the charge transfer band at ~400 nm, a d-d band was observed at 450 nm (λmax : 22.222 cm^{-1}, ε: 582450 mol^{-1} cm^{-1}) and is due to dz^2---> dx^2—y^2 transition. A very significant blue shift observed in the d-d band for (**3**) compared to (**1**) and (**2**) is due to the presence of strong field cyanide donor around nickel. Presence of cyanide ligand increases the LFSE and hence electronic transition to highly antibonding dx^2—y^2 orbital is observed at lower wavelength.

3.2. Cyclic voltammetry

All the complexes show metal centered reduction as reported earlier [7]. Figs. 1 and 2 show the one-electron reductions corresponding to Ni(II) → Ni(I) for two representative complexes. All the reductions have been found to be irreversible. In all the reductions leading to the formation of Ni(I) complex, the reduced species is highly unstable undergoing decomposition as is indicated by the complete irreversibility of the processes. The observed process is an electrochemical reduction followed by chemical decomposition. The Ni(I) complexes produced by the electrochemical reduction are of very short life time and decompose chemically and hence could not be identified in the reverse cycle. All the phosphine complexes show similar reduction potentials because of almost identical environment around nickel. However, reduction potential of the parent complex is much larger than those of the mixed ligand complexes due to the greater π-accepting ability of the phosphines [18]. Following is the increasing trend of reduction potentials (mV): -1501(**2**) < -1510(**1**) < -1512 (**3**) << -1604 $[Ni(pipdtc)_2]$.

3.3. Crystal structures

ORTEP diagram of complex (**1**) is shown in Fig. 3. The molecule is a discrete mononuclear unit, which has no significant intermolecular contacts. The planar diamagnetic complex contains NiS_2PN chromophore. Two formula units are present in the unit cell. The Ni—S bond distances, 2.227(1) and 2.172(1) Å are significantly different due to the difference in trans influence exerted by phosphine and NCS anion. The thioureide C—N distance observed in the compound is 1.289(3) Å, which is shorter than the distance observed in the parent $[Ni(pipdtc)_2]$ (1.327(5) Å) [14]. The Ni—P and Ni—N distances are 2.209(1) and 1.865(2) Å respectively. The S—Ni—S bite angle is 78.58(4)° which is not quite different from that observed in the parent dithiocarbamate. The P—Ni—N angle (94.3(1)°) indicates the planar conformation of the complexes. The Ni—N—C angle (176.3(3)°) indicates small deviation from linearity and is due to the steric effect of bulky phosphine ligands. The bond parameters of the dithiocarbamate moiety are found to be normal.

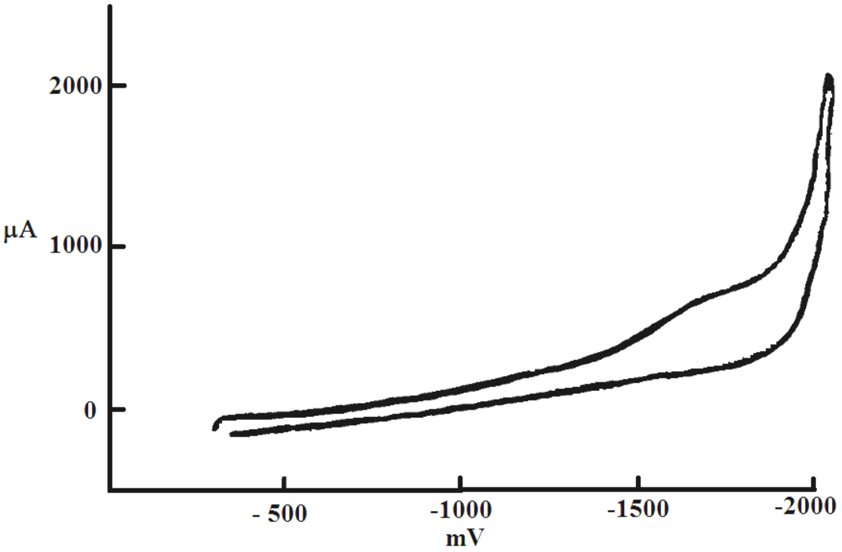

Figure 1. Cyclic voltammogram of $[Ni(pipdtc)_2]$.

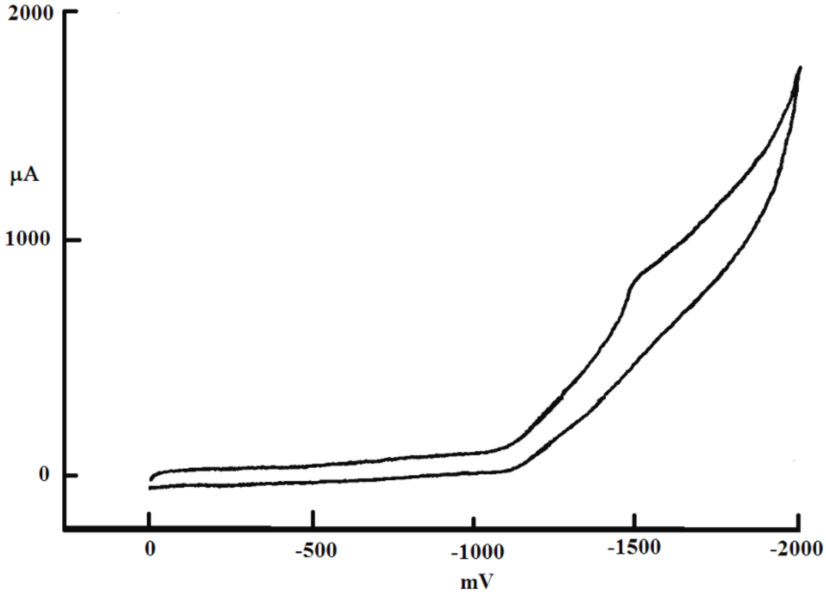

Figure 2. Cyclic voltammogram of $[Ni(pipdtc)(PPh_3)(NCS)]$.

ORTEP of (**2**) is shown in Fig. 4. Two formula units are present in the unit cell. The mononuclear units show no significant intermolecular contacts. The diamagnetic complex contains planar NiS_2PN chromophore. The Ni—S bond distances, 2.182(1) and 2.206(1) Å are significantly different, due to the trans influences exerted by phosphine and NCS. PPh_3 being a good π-acceptor has a greater trans influence and, hence the Ni—S bond trans to P is longer than the one trans to NCS anion. Asymmetry in the Ni—S bonds leads to an increase in Ni—S—C angle (86.64(7)°) and a contraction in S—C—S angle (108.0(1)°). The C—N(thioureide) distance 1.303(2) Å, is significantly different from that of the parent $[Ni(pipdtc)_2]$ (1.327(5) Å) [14], indicating the mesomeric drift of electron density from the S_2CN group towards the metal atom. The Ni—P and Ni—N distances are 2.213(1) and 1.871(2) Å respectively. The S—Ni—S angle is found to be 78.67(3)°, which is similar to the angle observed in the parent dithiocarbamate viz, 79.4(1)°. The P—Ni—N angle indicates the near planar conformation of the complex. The Ni—N—C angle (163.5(2)°) indicates deviation from linearity to a larger extent compared to that observed in (**1**) due to the steric effect of the 4-methyl group.

ORTEP of (**3**) is shown in Fig. 5. The complex is monomeric without any significant intermolecular contacts. The complex contains planar NiS_2PC chromophore. Two formula units are present in the unit cell. The Ni—S distances are 2.199(1) and 2.206(1) Å and PPh_3 shows a higher π-accepting

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

(1)		(2)		(3)	
Ni(1)—S(2)	2.227(1)	Ni(1)—S(2)	2.206(1)	Ni(1)—S(2)	2.206(1)
Ni(1)—S(3)	2.172(1)	Ni(1)—S(3)	2.182(1)	Ni(1)—S(3)	2.199(1)
Ni(1)—P(13)	2. 209(1)	Ni(1)—P(13)	2.213(1)	Ni(1)—P(13)	2.203(1)
Ni(1)—N(10)	1.865(2)	Ni(1)—N10	1.871(2)	Ni(1)—C(11)	1.936(4)
S(2)—C(4)	1.723(2)	S(2)—C(4)	1.709(2)	S(2)—C(4)	1.725(4)
S(3)—C(4)	1.732(3)	S(3)—C(4)	1.730(2)	S(3)—C(4)	1.706(4)
C(4)—N(5)	1.289(3)	C(4)—N(5)	1.303(2)	C(4)—N(5)	1.313(5)
N(10)—C(11)	1.148(3)	N(10)—C(11)	1.150(2)	C(11)—N(12)	1.413(5)
C(11)—S(12)	1.618(3)	C(11)—S(12)	1.623(2)	N(5)—C(6)	1.160(6)
N(5)—C(35)	1.468(3)	N(5)—C(43)	1.473(3)	N(5)—C(10)	1.466(5)
P(13)—C(14)	1.820(2)	P(13)—C(14)	1.823(2)	P(13)—C(14)	1.822(2)
S(2)—Ni(1)—S(3)	78.58(4)	S(2)—Ni(1)—S(3)	78.67(3)	S(2)—Ni(1)—S(3)	78.8(1)
S(2)—Ni(1)—N(10)	93.9(1)	S(2)—Ni(1)—N(10)	91.4(1)	S(2)—Ni(1)—C(11)	89.9(1)
N(10)—Ni(1)—P(13)	94.3(1)	N(10)—Ni(1)—P(13)	93.8(1)	C(11)—Ni(1)—P(13)	95.5(1)
S(3)—Ni(1)—P(13)	93.32(4)	S(3)—Ni(1)—P(13)	96.07(3)	S(2)—Ni(1)—P(13)	95.7(1)
S(2)—C(4)—S(3)	107.5(1)	S(2)—(C4)—S(3)	108.0(1)	S(2)—C(4)—S(3)	109.2(2)
S(2)—C(4)—N(5)	127.0(2)	S(2)—C(4)—N(5)	126.4(1)	S(2)—C(4)—N(5)	125.0(3)
S(3)—C(4)—N(5)	125.5(2)	S(3)—C(4)—N(5)	125.6(1)	S(3)—C(4)—N(5)	125.8(3)
C(4)—N(5)—C(35)	122.5(2)	C(4)—N(5)—C(34)	122.2(2)	C(4)—N(5)—C(6)	123.2(3)
Ni(1)—N(10)—C(11)	176.3(3)	Ni(1)—N(10)—C(11)	163.5(2)	Ni(1)—C(11)—N(12)	174.1(2)
N(10)—C(11)—(S12)	178.9(3)	N(10)—C(11)—S(12)	178.9(2)	-	-

ability in the present case than the CN anion. The thioureide C—N distance is 1.313(5) Å, which is shorter than the distance observed in its parent, 1.327(5) Å [14]. The observed reduction in bond length is due to the mesomeric drift of electrons from the dithiocarbamate moiety towards nickel atom. The Ni—P and Ni—C distances are 2.203(2) Å and 1.936(4) Å, respectively. The S—Ni—S bite angle is 78.8 (1)°, which is similar to that observed in the parent dithiocarbamate. The P—Ni—C angle (95.5(1)°) indicates the near planar geometry of the complex. The Ni—C—N angle is 174.1(2)°, which indicates considerable deviation from linearity. The complex crystallizes with a molecule of acetonitrile which showed extensive disorder (Hydrogens associated with the solvent molecule could not be located). Important parameters of related compounds are compared in Table 3.

3.4. Bond valence sum (BVS) analysis

Bond valence sum (BVS) analysis has been used to determine the oxidation state of metal ions in solids based on crystallographically determined M—L bond distances [19-21]. Calculation of BVS involves the relationship for the valence v_{ij} of a bond between two atoms i and j as $v_{ij} = \exp[(r_o - r)/B]$, where ‘r’ is the crystallographically determined bond length, ‘B’ is taken to be a universal

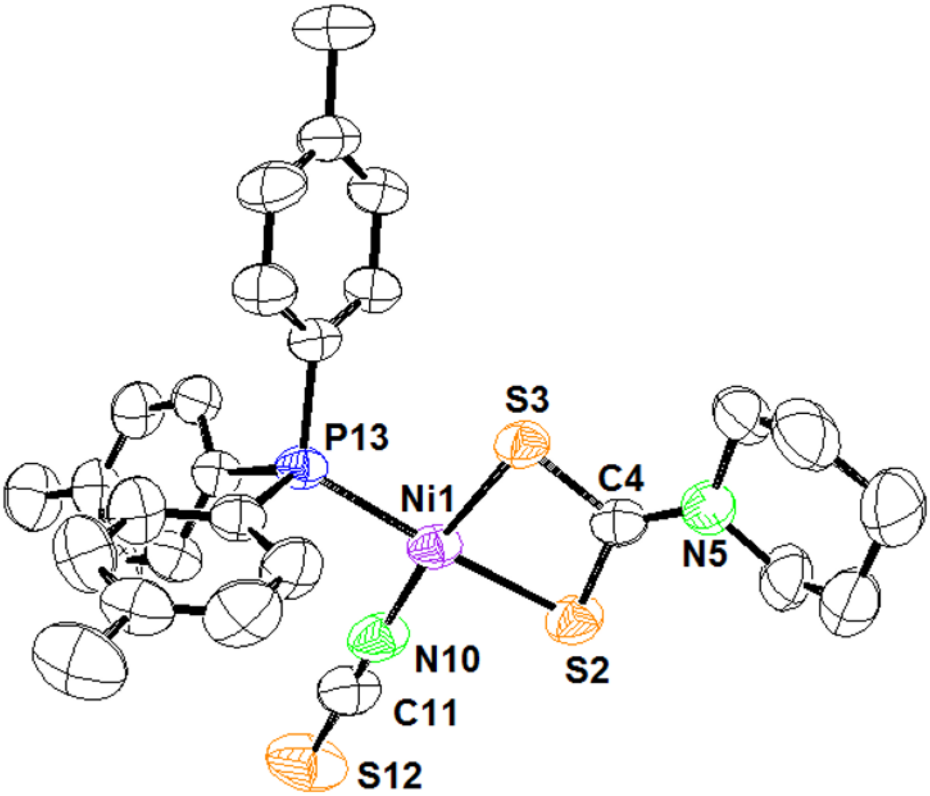

Figure 3. ORTEP of [Ni(pipdtc)(4-MP)(NCS)] (1) (Hydrogens are excluded; Ellipses are of 50% probability).

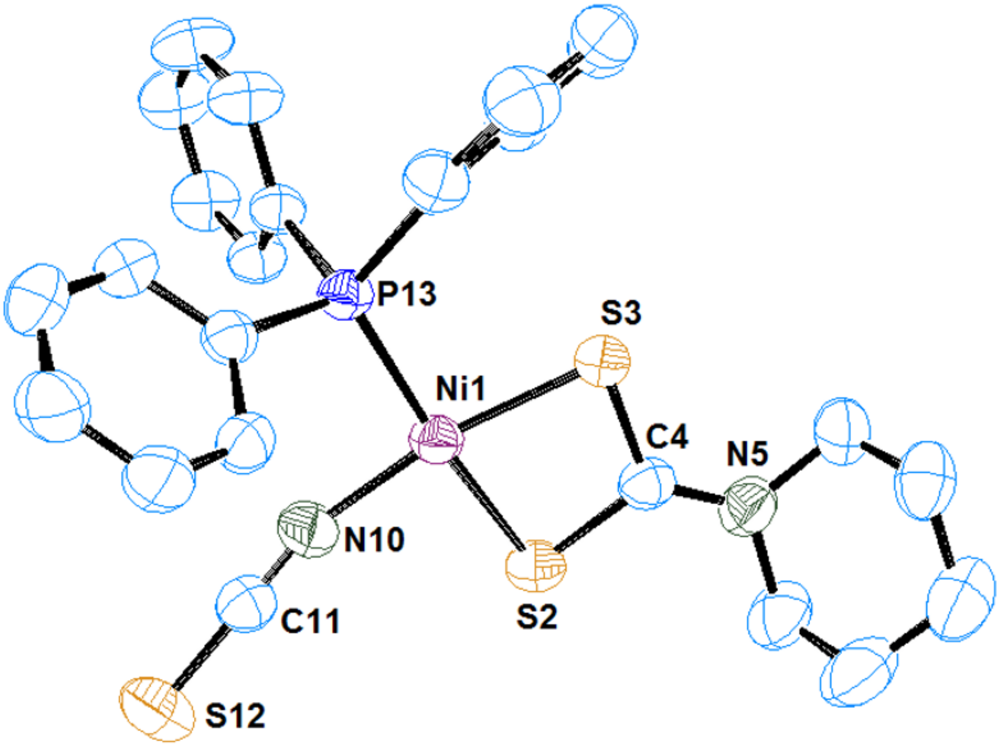

Figure 4. ORTEP of [Ni(pipdtc)(PPh_3)(NCS)] (2) (Hydrogens are excluded; Ellipses are of 50% probability).

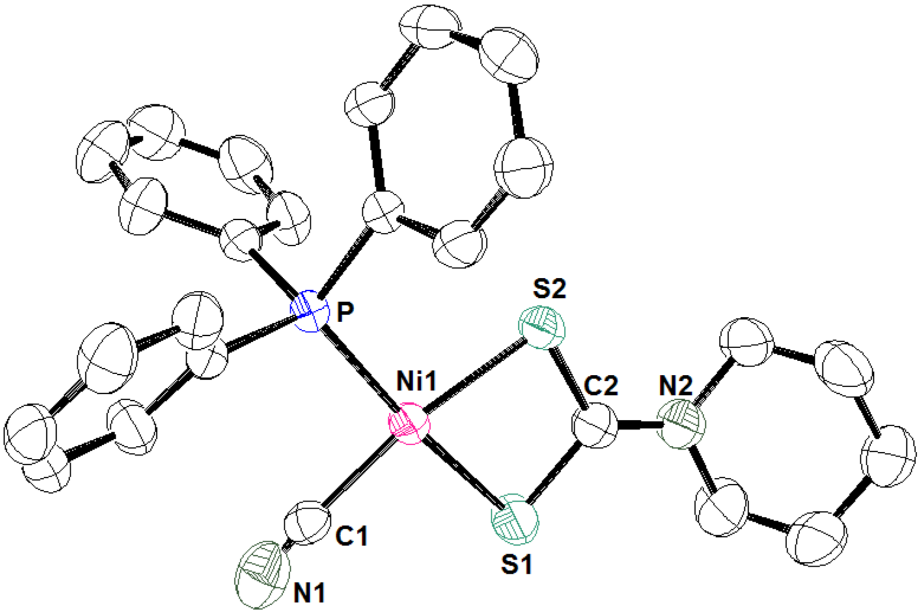

Figure 5. ORTEP of [Ni(pipdtc)(PPh$_3$)(CN)] (3) (Hydrogens are excluded; Ellipses are of 50% probability).

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

Compound	Ni—S(1)	Ni—S(2)	Ni—P(1)	Ni—P(2)	C—N	Ni—N/ Ni—C	S—Ni—S	P—Ni—N/ P—Ni—C	Ref.
[Ni(pipdtc)$_2$]	2.207(1)	2.196(1)	-	-	1.327(5)	-	79.4(0)	-	[14]
[Ni(pipdtc)(PPh$_3$)$_2$]$^+$	2.192(1)	2.225(1)	2.201(1)	2.229(1)	1.284(5)	-	78.2(1)	-	[21]
[Ni(pipdtc)(1,3-dppp)]$^+$	2.216(4)	2.206(4)	2.177(4)	2.179(4)	1.322(6)	-	79.2(1)	-	[22]
[Ni(pipdtc)(1,4-dppb)]$^+$	2.217(2)	2.213(2)	2.209(2)	2.197(2)	1.272(10)	-	78.34(9)	-	[23]
[Ni(pipdtc)(4-MP)(NCS)]	2.227(1)*	2.172(1)	2.209(1)	-	1.289(3)	1.865(2)	78.58(4)	94.3(1)	This work
[Ni(pipdtc)(PPh$_3$)(NCS)]	2.206(1)*	2.182(1)	2.213(1)	-	1.303(3)	1.871(2)	78.67(3)	93.8(1)	This work
[Ni(pipdtc)(PPh$_3$)(CN)]	2.206(1)*	2.199(1)	2.203(1)	-	1.313(5)	1.936(4)	78.82(4)	95.5(1)	This work

**Ni—S bond trans to Ni—P*

Table 4. Values of r_o used to calculate Bond Valence Sums.

Bond	r_o/Å $^{a)}$	r_o/Å
Ni—S	2.059	1.937$^{b)}$
Ni—N	1.743	1.647$^{b)}$
Ni—P	2.128	1.884$^{c)}$
Ni—C	1.818	1.604$^{c)}$

$^{a)}$[19,20] $^{b)}$ [21] $^{c)}$$r_o$ for Ni-C and Ni-P are reported from a fit of experimental bond distances for twenty complexes with divalent nickel as the central metal [23-25]

constant equal to 0.37 and r_o is the empirically determined bond valence parameter. The sum of the individual values of v_{ij} for the j bond around a central metal gives the BVS, $\Sigma\, v_{ij} = V_i$, which is generally close to the formal oxidation state of the metal [19,20]. Table 4 lists the r_o values used in the present calculation and the values of BVS calculated are given in Table 5. BVS calculated by the use of r_o obtained by OK/B method [19,20] for divalent nickel complexes always resulted in a higher V_i, *i.e.*, a higher value than the formal oxidation state of +2. For many of the dithiocarbamate complexes of nickel (II), the bond valence sums exceeded 2.8. To overcome the discrepancy, r_o values have been re-determined for some model complexes of transition metals from our data [22-25]. BVS values obtained for the complexes with the re-determined r_o resulted in values closer to 2 confirming the oxidation state of nickel.

The neutral isothiocyanato complexes have higher BVS than the ionic phosphine complexes due to variations in the metal – ligand bond distances and are comparable to the BVS of parent bisdithiocarbamate. The cationic complexes have relatively lower values as

Table 5. Bond Valence Sums (BVS) for divalent nickel complexes.

Compound	BVS$^{a)}$	BVS$^{b)}$	Ref.
[Ni(pipdtc)$_2$]	3.005	1.957	[14]
[Ni(pipdtc)(PPh$_3$)$_2$]$^+$	2.919	1.779	[21]
[Ni(pipdtc)(1,3-dppp)]$^+$	3.073	1.857	[22]
[Ni(pipdtc)(1,4-dppb)]$^+$	2.944	1.763	[23]
[Ni(pipdtc)(4-MP)(NCS)]	2.892	1.949	This work
[Ni(pipdtc)(PPh$_3$)(NCS)]	2.885	1.948	This work
[Ni(pipdtc)(PPh$_3$)(CN)]	2.896	1.803	This work

$^{a)}$ *use of r_o reported in the literature [19,20]*
$^{b)}$ *use of r_o re-determined [23-25]*

quoted from the literature. The bond valence parameters reported for the present complexes clearly confirm the formal oxidation state of nickel to be +2.

4. Conclusions

The Ni—S distances in the complexes (**1**), (**2**) and (**3**) are distinctly different and the observed asymmetry is due to differences in trans influences exerted by phosphine, NCS$^-$ and CN$^-$. Ni—S bond distances trans to PPh$_3$/4-MP are observed to be in the following order: (**1**) > (**2**) ~ (**3**). Ni—S bond distances trans to NCS/CN follow: (**3**) > (**2**) > (**1**). The trans influence in divalent nickel complexes is clearly established by the observation. Particularly, 4-MP shows a highly significant trans influence than triphenylphosphine on Ni-S bond. Similarly, CN$^-$ exerts a marginally significant higher trans influence compared to NCS$^-$. The thioureide C—N distances in the mixed ligand complexes are relatively very short compared to the parent compound due to the mesomeric drift of electron density towards the metal. The Ni—N—C angle (163.5(2)°) observed in (**2**) indicates deviation from linearity to a larger extent compared to that observed in (**1**) (176.3(3)°) due to the steric effect of the 4-methyl group However, the presence of π-acids, PPh$_3$ and 4-MP alleviate the electron density on the nickel atom in solution and, hence the reduction potentials for the mixed ligand complexes are much less compared to the parent NiS$_4$ chromophore.

Supplementary material

CCDC 183258 (for **1**), 238328 (for **2**) and 210917 (for **3**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge *via* 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 336033; or deposit@ccdc.cam.ac.uk).

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References

[1] V.K. Jain, S. Chaudhury, Polyhedron 5, 1685 (1996)
[2] P.S. Jarrett, O.M.N. Dhubhghaill, P.J. Sadler, J. Chem. Soc., Dalton Trans. 1863 (1993)
[3] A.H. Norbury, Adv. Inorg. Chem. 17, 231 (1975)
[4] K. Ramalingam, G. Aravamudan, V. Venkatachalam, Bull. Chem. Soc. Japan 66 , 1554 (1993)
[5] J.A. Mc Cleverty, N.J. Morrison, J. Chem. Soc., Dalton Trans. 541 (1976)
[6] R.P. Burns, F.P. McCullough, C.A. McAuliffe, Adv. Inorg. Chem. Radiochem 23, 211 (1980)
[7] K. Ramalingam, G. Aravamudan, M. Seshasayee, Inorg. Chim. Acta 128, 231(1987)
[8] A. Manohar, K. Ramalingam, R. Thiruneelakandan, G. Bocelli, L. Righi, Z. Anorg. Allg. Chem. 632, 461 (2006)
[9] R. Thiruneelakandan, K. Ramalingam, G. Bocelli, L. Righi, Z. Anorg. Allg. Chem. 631, 187 (2005)
[10] B. Arul Prakasam, K. Ramalingam, G. Bocelli, A. Cantoni, Bull. Chem. Soc. Japan 79, 113 (2006)
[11] S. Srinivasan, K. Ramalingam, C. Rizzoli, Polyhedron. 33, 60 (2012)
[12] R. Baskaran, K. Ramalingam, G. Bocelli, A. Cantoni, C. Rizzloi, J. Coord. Chem. 61, 1710 (2008)
[13] B. Arul Prakasam, K. Ramalingam, G. Bocelli, R.Olla, Z. Anorg. Allg. Chem. 630, 301 (2004)
[14] P.W.G. Newman, C.L. Raston, A.H. White, J. Chem. Soc. Dalton Trans. 1332 (1973)
[15] Software for structure solution in Bruker AXS software - SHELXTL-NT V5.1 (Bruker AXS Inc., Madison, USA, 1999)
[16] L.J. Farrugia, ORTEP-3 for Windows (University of Glassgow, Scotland, UK, 1999)
[17] F. Bonati, R. Ugo, J. Organomet. Chem. 110, 257 (1967)
[18] G. Bontempelli, F. Magno, L. Schiavon, B. Corain, Inorg. Chem. 20, 2579 (1981)
[19] I.D. Brown, D. Altermatt, Acta Crystallogr. B41, 244 (1985)

[20] M.O. Keeffe, N.E. Brese, J. Am. Chem. Soc. 113, 3226 (1991)
[21] W. Liu, H.H. Thorp, Inorg. Chem. 32, 4102 (1993)
[22] V. Venkatachalam, K. Ramalingam, T.C.W. Make, L. Bao-sheng, Polyhedron 12, 1289 (1996)
[23] A. Manohar, K. Ramalingam, R. Thiruneelakandan, G. Bocelli, L. Righi, Z. Anorg. Allg. Chem. 627, 1103 (2001)
[24] R. Thiruneelakandan, K. Ramalingam, A. Manohar, G. Bocelli, L. Righ, Z. Anorg. Allg. Chem. 628, 685 (2002)
[25] R. Baskaran, K. Ramalingam, R. Thiruneelakandan, B. Arul Prakasam, G. Bocelli, A. Cantoni, J. Coord. Chem. 62, 1076 (2009)