Synthesis, Spectral, Valence-Bond Parameters, and Single Crystal X-ray Structural Studies on [Ni(dnpdtc)(PPh$_3$)(NCS)] and [Ni(dnpdtc)(PPh$_3$)(CN)]

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Abstract. Two new nickel complexes withplanar surrounding of Ni [Ni(dnpdtc)(PPh$_3$)(NCS)] **(1)** and [Ni(dnpdtc)(PPh$_3$)(CN)] **(2)** (dnpdtc=N,N-dipropyldithiocarbamate) were prepared from the parent dithiocarbamate and were characterized by elemental analysis, electronic, IR and NMR spectra. The structures of both the complexes were determined by single crystal X-ray crystallography. Thioureide stretching vibrations occur at 1528 cm^{-1} and 1521 cm^{-1} for **1** and **2** respectively. Large ^{31}P chemical shifts were observed for the two compounds. A significant asymmetry in Ni−S bond distances was observed in compound **1** [2.1700(16) and 2.2251(17)Å] whereas in compound **2** the bond distances were almost similar [2.2100(14) and 2.2122(13)Å]. A marginal difference was observed with respect to the thioureide bond distances [1.340(6)Å for **1** and 1.312(5)Å for **2**]. The observation clearly supports the less effective trans influence of SCN$^-$ over PPh$_3$. However, PPh$_3$ and CN$^-$ show almost similar trans influence.

Keywords: Nickel; Dithiocarbamate; Crystal structure; Triphenylphosphine; NMR spectroscopy

Synthese, Spektroskopie, Bindungs-Valenz-Parameter und Einkristallstrukturuntersuchungen von [Ni(dnpdtc)(PPh$_3$)(NCS)] und [Ni(dnpdtc)(PPh$_3$)(CN)]

Inhaltsübersicht. Zwei neue Nickelkomplexe mit planarer Umgebung an den Ni-Atomen, [Ni(dnpdtc)(PPh$_3$)(NCS)] (**1**) und [Ni(dnpdtc)(PPh$_3$)(CN)] (**2**) (dnpdtc = N,N-dipropyldithiocarbamat), wurden aus [Ni(dnpdtc)$_2$] hergestellt und durch Elementaranalysen, elektronischen, IR- und NMR-Spektren charakterisiert. Die Strukturen beider Komplexe wurden durch Einkristallstrukturanalysen röntgenographisch ermittelt. Die CN-Valenzschwingungen der Dithiocarbamatgruppen liegen bei 1528 cm^{-1} (**1**) und 1521 cm^{-1} (**2**). In den ^{31}P-NMR-Spektren werden große chemische Verschiebungen beobachtet. Die Ni−S-Bindungen in **1** sind mit 2,170(2) und 2,225(2) Å signifikant verschieden, während sie in **2** mit 2,210 und 2,212(1) Å nahezu gleich sind. Die CN-Abstände der Dithiocarbamatliganden sind mit 1,340(6) Å (**1**) und 1,312(5) Å (**2**) nur marginal verschieden. Dies bestätigt den gegenüber PPh$_3$ geringeren Transeinfluß von SCN$^-$ und den nahezu gleich großen Transeinfluß von PPh$_3$ und CN$^-$.

Introduction

Dithiocarbamate ligands (dtc) display a strong prospenity of binding to metal atoms such as nickel [1−4]. The nickel complexes with phosphine ligands have been studied for their anti-cancer activity [5]. Group VIII dithiolates containing planar MS$_4$ chromophores show variable behaviour in their reactions with Lewis bases. Unlike it's congeners Ni^{II} is a borderline acceptor and it's planar dithiocarbamate ligand prefers to react with soft Lewis bases such as phosphines over hard nitrogenousbases. Nickel(II) dithiocarbamates in their reaction with PR$_3$ form planar NiS$_2$P$_2$ chromophores [6, 7]. Synthetic and structural studies on [Ni(dtc)Cl(PPh$_3$)], [Ni(dtc)(PPh$_3$)$_2$](ClO$_4$) and [Ni(dtc)(dppe)](BPh$_4$) where dtc=S$_2$CN(C$_2$H$_5$)$_2$, S$_2$CNH(C$_2$H$_4$OH), S$_2$CN(C$_2$H$_4$OH)$_2$, S$_2$CN(C$_2$H$_5$)$_2$, S$_2$CN(C$_5$H$_{10}$) have been reported from our laboratory [1−3]. In order to understand the influence of SCN$^-$ and CN$^-$ donors on the coordination environment around nickel atom and on the thioureide bond, we report the synthesis, spectral and structural characterization of two new complexes [Ni(dnpdtc)(PPh$_3$)(NCS)] **(1)** and [Ni(dnpdtc)(PPh$_3$)(CN)] **(2)** where dnpdtc=N, N-dipropyldithiocarbamate in this paper.

Results and Discussion

IR spectral studies

IR spectra show ν(N-C) bands at 1528 cm^{-1} for **1** and 1521 cm^{-1} for **2** The shift in ν(N-C) values to higher wave number compared with parent [Ni(dnpdtc)$_2$] complex observed at 1508 cm^{-1} is due to the mesomeric drift of electron density from the dithiocarbamate ligand towards the metal atom and this increases the contribution of polar thioureide formin both the cases. The bands at higher wave number 2093

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Table 1 NMR Spectral data for 1 and 2. (Chemical shift values in ppm)

NMR[a)]	Compound	CH_3	α-CH_2	β-CH_2	Aromatic	Thioureide N-C	P	S−^{13}C−N	^{13}CN
^{1}H	**1**	0.81 (t) & 0.92 (t)	1.60 (m)	3.30 (t) & 3.49 (t)	7.26−7.73 (m)	−	−	−	−
	2	0.83 (t) & 0.93 (t)	1.65 (m)	3.39 (t) & 3.56 (t)	7.26−7.73 (m)	−	−	−	−
^{13}C[b)]	**1**	11.11	20.59	50.69 & 50.87	128.16−134.24	203.63	−	143.69	−
	2	11.11	20.64	50.01 & 50.87	128.57−134.32	205.21	−	−	~130
^{31}P	**1**	−	−	−	−	−	22.03	−	−
	2	−	−	−	−	−	30.28	−	−

a) $CDCl_3$ was used as solvent

b) ^{13}C NMR spectra were recorded in proton decoupled mode.

cm^{-1} for **1** and 2112 cm^{-1} for **2** indicate the presence of SCN$^-$ in **1** and CN$^-$ in **2** respectively. The ν(C-S) band appears at 1095 cm^{-1} for **1** and at 1094cm^{-1} for **2** without any splitting, supporting the bidentate coordination of the dithiocarbamate moiety [8].

NMR spectral studies

NMR spectra were recorded at room temperature using TMS as internal reference. The NMR chemical shift values are given in Table 1 with splitting pattern.

^{1}HNMR. For compound **1** as expected two sets of signals were obtained for the propyl group. The methyl group protons give two triplets at 0.81 and 0.92 ppm. The α-CH_2 protons appear as a collapsed multipletin the region of 1.60 ppm. In the downfield region, two sets of triplets at 3.30 and 3.49 ppm were obtained for β-CH_2 protons whereas in the case of complexes with NiS_2P_2 chromophore, only one set of signal was obtained for the propyl group. A multiplet in the region of 7.26−7.73 ppm was due to aromatic protons. For compound **2** also the signals were obtained with the same splitting pattern but with slight difference in chemical shift values.

^{13}C NMR. The most important chemical shift values of thioureide carbon atom ($S_2{}^{13}C$-N) were observed at 203.63 and 205.21 ppm for complexes **1** and **2**, respectively. The mesomeric shift of electron density from dithiocarbamate moiety towards the metal atom contributes to the upfield shift from the normal chemical shift value of [$Ni(dtc)_2$] complexes (206-210 ppm) [9]. The observation is supported by the higher ν(N-C) values observed for complexes **1** and **2** in the present study. For compound **1**, the low intensity signal at 143.69 ppm was assigned to carbon atom present in NCS moiety, whereas for compound **2**, the signal for cyanide carbon merged with that of the aromatic carbons.

^{31}P NMR. ^{31}P NMR spectra for compound **1** and **2** show signals at 22.03 and 30.28 ppm, respectively. In ^{31}P NMR, a large difference (~8.25 ppm) was observed, suggesting that the back bonding effects are felt more pronounced in **2**.

Bond-valence parameter calculations

For the two complexes values were calculated by two procedures [10, 11]. The values are 2.9931 (B/OK), 2.9456 (OK/B); 3.1117 (B/OK), 3.0715 (OK/B) for the two complexes **1** and **2**, respectively. For both the complexes, the values are higher than the expected formal oxidation state of +2. The higher value observed in the present set of compounds supports the fact that the Ni-S, Ni-P bonds are more covalent and the back bonding effects are very highly pronounced [12]. Between the SCN$^-$ and CN$^-$ donors, CN$^-$ appears to alleviate the electron density on the metal atom to a greater extent through back bonding leading to higher positive charge as suggested by the larger BVS values.

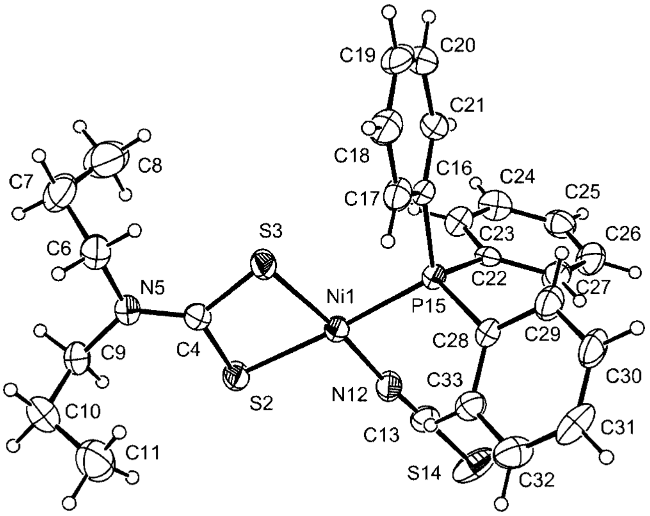

Fig. 1 ORTEP diagram of [$Ni(dnpdtc)(PPh_3)(NCS)$]

Structural analysis

The ORTEP diagram of **1** is shown in Figure 1. The complex is monomeric and discrete. Four units of [$Ni(dnpdtc)(PPh_3)(NCS)$] are present in the unit cell. Because of the small bite angle associated with the dithiocarbamate moiety [78.75(6)°], the NiS_2PN chromophore is not of perfect square planar arrangement. The planarity of the surrounding of Ni atoms is inkeeping with the observed diamagnetism of the complex.The short thioureide N-C distance, 1.340(6)Å indicates that the π electron density is delocalized over S_2CN moiety and that this bond has a strong double bond character. This is also confirmed by the fact

Table 2 Crystal data, data collection and refinement parameters for [Ni(dnpdtc)(PPh_3)(NCS)] (1) and [Ni(dnpdtc)(PPh_3)(CN)] (**2**)

	[Ni(dnpdtc)(PPh_3)(NCS)]	**[Ni(dnpdtc)(PPh_3)(CN)]**
Empirical formula	$C_{26}H_{29}N_2NiPS_3$	$C_{26}H_{29}N_2NiPS_2$
FW	555.4	523.3
Crystal dimensions (mm)	0.21 x 0.23 x 0.34	0.17 x 0.28 x 0.31
Crystal system	monoclinic	triclinic
Space group	P21/n	$P\bar{1}$
a/Å	8.310(3)	10.364 (2)
b/Å	20.433 (3)	14.160 (3)
c/Å	16.963 (2)	9.918 (3)
α/°	90	94.76 (2)
β/°	104.18 (2)	105.28 (3)
γ/°	90	111.00 (3)
Diffractometer	Phillips PW 100	Enraf Nonius CAD 4
Temperature	293K	293K
U/ $Å^3$	2792.5 (11)	1285.1 (5)
Z	4	2
Dc/g cm^{-3}	1.321	1.352
μ/cm^{-1}	9.93	3.312
F(000)	1160	548
λ/Å	Mo − Kα (0.71069)	Mo − Kα (0.71069)
θ range/°	3.08−27.05	3.41−69.98
Scan type	ω−2θ	ω−2θ
Index ranges	$-0 \le h \le 10, 0 \le k \le 26, -21 \le l \le 20$	$-12 \le h \le 11, -17 \le k \le 17, 0 \le l \le 12$
Reflections collected	6094	4858
Observed reflections $F_0 > 4\sigma(F_0)$	1911	3235
Weighting scheme	$W = 1/[\sigma^2(F_0^2) + (0.0215\ P)^2 + 0.00\ P]$ where $P = (F_0^2 + 2\ F_c^2)/3$	$W = 1/[\sigma^2(F_0^2) + (0.1198\ P)^2 + 0.00\ P]$ where $P = (F_0^2 + 2\ F_c^2)/3$
Number of parameters refined	414	443
Final R, R_w (obs, data)	0.0584, 0.0647	0.0541, 0.1421
GOOF	0.780	0.872

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre (211256 & 211257 for **1** and **2**, respectively). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

Table 3 Selected bond distances/Å and angles/° for [Ni(dnpdtc)(PPh_3)(NCS)] (**1**) and [Ni(dnpdtc)(PPh_3)(CN)] (**2**)

[Ni(dnpdtc)(PPh_3)(NCS)]		**[Ni(dnpdtc)(PPh_3)(CN)]**	
Ni1-S3	2.170(2)	Ni1-S3	2.210(1)
Ni1-S2	2.225(2)	Ni1-S2	2.212(1)
Ni1-N12	1.854(5)	Ni1-C12	1.861(4)
Ni1-P15	2.198(2)	Ni1-P15	2.184(1)
S2-C4	1.699(5)	S2-C4	1.719(4)
S3-C4	1.722(6)	S3-C4	1.735(4)
N5-C4	1.340(6)	N5-C4	1.312(5)
N5-C9	1.486(8)	N5-C6	1.468(6)
N5-C6	1.474(8)	N5-C9	1.472(6)
C6-C7	1.501(11)	C6-C7B	1.41(217)
C7-C8	1.479(12)	C6-C7A	1.66(2)
C9-C10	1.506(11)	C7A-C7B	0.676(14)
C10-C11	1.518(12)	C7A-C8B	1.01(2)
N12-C13	1.148(6)	C7A-C8A	1.48(2)
C13-S14	1.631(6)	C12-N13	1.141(5)
N12-Ni1-S3	174.2(2)	C12-Ni1-P15	95.11(13)
N12-Ni1-P15	90.40(2)	C12-Ni1-S3	171.12(13)
S3-Ni1-P15	95.42(6)	P15-Ni1-S3	93.73(6)
N12-Ni1-S2	95.50(2)	C12-Ni1-S2	92.30(13)
S3-Ni1-S2	78.75(6)	P15-Ni1-S2	167.56(5)
P15-Ni1-S2	173.85(7)	S3-Ni1-S2	78.85(5)
C4-S2-Ni1	85.4(2)	C4-S2-Ni1	85.71(14)
C4-S3-Ni1	86.6(2)	C4-S3-Ni1	85.40(14)
N5-C4-S2	126.4(5)	N5-C4-S2	125.8(3)
N5-C4-S3	124.4(4)	N5-C4-S3	125.3(3)
S2-C4-S3	109.2(3)	S2-C4-S3	108.8(2)

that the two S-C-N angles [124.4(4) and 126.4(5)°] are much greater than that of S-C-S angle, 109.2(3)°.

In the isothiocyanate part, the N-C-S band angle is 179.1(6)° is . The C-N bond distance in N-C-S [1.148(6)Å] is shorter than that of thioureide N-C bond distance of 1.340(6)Å. The C-S bond length is 1.631(6)Å which is similarto C=S distance of 1.69 Å. Phenyl rings show normal bond parameters. The P-Ni-P angle in [Ni(dnpdtc)$(PPh_3)_2$]ClO_4 is 98.41(4)° whereas in compound **1** P-Ni-N bond angle is 90.39(15)°. The decrease of about 8° indicates that there is less steric crowding in **1** by the replacement of PPh_3 by NCS.

[Ni(dnpdtc)(PPh_3)(CN)] (**2**) is monomeric with two molecules per unit cell. The ORTEP diagram of the molecule is shown in Figure 2. The nickel atom has approximately planar surrounding, in keeping with the observed diamagnetism. The small bite angle of 78.85(5)° is observed in this case, which is in agreement with the values of complexes, which are reported earlier. The Ni-S [2.2100(1) and 2.2122(1)Å] and C-S [1.719(4) and 1.735(4)Å] bonds are almost symmetric, indicating that the negative charge on the dithiocarbamate ligand is equally distributed all over the donor atoms. The short thioureide N-C distance of 1.312(5)Å is due to delocalized electron density over the S_2CN moiety and this bond has a partial double bond character. The C-N bond length of 1.141(5)Å exemplifies the triple bond character.

Comparison of **1** and **2** shows that S-Ni-S bite angles [79.75(6) vs 78.85(5)°] and the Ni-S-C angles [86.0 vs 85.55°] are very similar. The C-N bond length in N-C-S

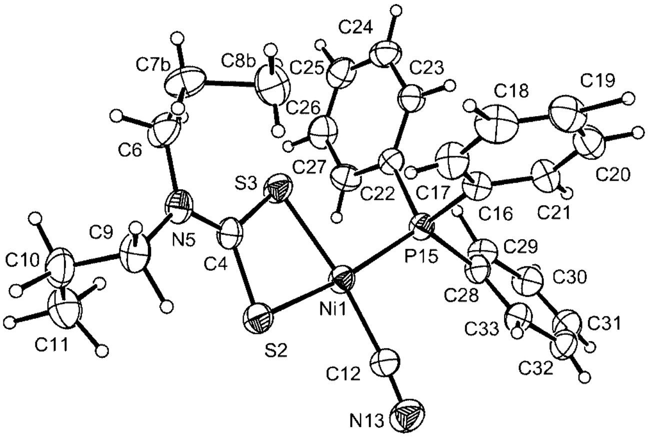

Fig. 2 ORTEP diagram of [Ni(dnpdtc)(PPh_3)(CN)]

moiety of **1** [1.148(6)°] is comparable with the C-N bond length of **2**. For compound **1**, the asymmetry in Ni-S distances [2.170(2) and 2.225(2)Å] was observed. The C-S bond lengths are also asymmetric [1.699(5) and 1.722(6)Å]. This asymmetry shows that the negative charge is not equally spread over all the donor atoms. Thioureide bond distances in **1** and **2** are characteristic of partial double bond nature indicating the mesomeric drift of electron density from N towards the metal ion. Compound **2** shows an apparently lower ν(N-C) value than that observed for **1** however, crystallographically N-Cbond distance observed in **2** is significantly shorter than that in compound **1**. In the light of the observed bond distances around nickel, SCN^- exerts a less effective trans influence over PPh_3 on the Ni-S bonds.

Experimental

All the reagents and solvents employed were commercially available analytical grade materials used as supplied, without further purification. IR spectra were recorded on ABB Bomem MB 104 spectrophotometer (range 4000−400 cm^{-1}) as KBr pellets. The electronic spectra were recorded in CH_2Cl_2 on a HITACHI U-2001 spectrophotometer. NMR spectra were recorded on Brucker AMX-400 spectrometer at room temperature, using $CDCl_3$ as solvent.

Preparation of complexes

(N,N-Dipropyldithiocarbamato)(isothiocyanato)(triphenylphosphine) nickel(II). [Ni(dnpdtc)(PPh_3)(NCS)] **(1)**. A mixture of $Ni(dnpdtc)_2$ (210 mg, 0.5 mmol), PPh_3 (260 mg, 1 mmol), $NiCl_2{\cdot}6H_2O$ (120 mg, 0.5 mmol) and NH_4SCN (75 mg, 1 mmol) was refluxed for 3h in methanol-acetonitrile solvent mixture (50:50, 50 cm^3) and was then concentrated to ca 25 cm^3. The dark purple-red solution obtained was filtered and was kept for evaporation. After 3 days, fine single crystals suitable for X-ray structural analysis were obtained. (Yield 70%, 400 mg, dec. 185°C). $C_{26}H_{29}N_2NiPS_3$ (555.4); C 55.93 (calc. 56.23); H 5.09 (5.26); N 4.93 (5.04) %.

(Cyano)(N,N-dipropyldithiocarbamato)(triphenylphosphine)-nickel(II). A mixture of $Ni(dnpdtc)_2$ (210 mg, 0.5 mmol), PPh_3 (260 mg, 1 mmol), $NiCl_2{\cdot}6H_2O$ (120 mg, 0.5 mmol) and KCN (65 mg, 1 mmol) was refluxed for 4h in methanol-dichloromethane solvent mixture (50:50, 50 cm^3) and was then concentrated to ca 25 cm^3. The pale orange-red solution obtained was filtered and was kept for evaporation. After 2 days orange-red solid separated out. Single crystals suitable for X-ray structural analysis were obtained by repeated recrystallization from methanol-dichloromethane solvent mixture. (Yield 65%, 370 mg, dec. 173°C) $C_{26}H_{29}N_2NiPS_2$ (523.3); C 58.91 (calc. 59.67); H 5.50 (5.58); N 5.18 (5.34) %.

X-ray crystallography

Details of the crystal data, data collection and refinement parameters for **1** and **2** are summarized in Table 2. The structure was solved by direct methods using SHELXS-97 [13] and was refined by SHELX-97 [14]. All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were refined isotropically. Selected bond lengths and bond angles are given in Table 3.

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