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# Effect of free and chelating phosphine coordination environments on the NiS<sub>2</sub>P<sub>2</sub> chromophore: synthesis, NMR and other spectral studies. Crystal and molecular structures of (N,N-dipropyldithiocarbamato)di(triphenylphosphine)nickel(II) perchlorate and (N,N-dipropyldithiocarbamato)1,2bis((diphenylphosphino)ethane)nickel(II) tetraphenylborate

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#### Abstract

Planar [Ni(dnpdtc)(PPh<sub>3</sub>)<sub>2</sub>] ClO<sub>4</sub> · PPh<sub>3</sub> (1) and [Ni(dnpdtc)(dppe)]BPh<sub>4</sub> · H<sub>2</sub>O (2) (dnpdtc = *N*,*N*-dipropyldithiocarbamate, dppe = 1,2-bis(diphenylphosphino)ethane) complexes were prepared and characterized by elemental analysis, electronic, IR and NMR spectra and their structures were determined by single crystal X-ray crystallography. Both the complexes were diamagnetic. IR spectra of the two compounds show isobidentate coordination of the dithiocarbamate moiety. The important stretching mode characteristic of the thioureide bond occurs at 1536 and 1526 cm<sup>-1</sup> for 1 and 2, respectively. The BVS data support the highly covalent nature of the Ni–S interaction. NMR spectra of the complexes show very large (~20 ppm)<sup>31</sup>P chemical shifts in both compounds. The most important N<sup>13</sup>CS<sub>2</sub> chemical shifts appear at 199.17 and 201.88 ppm for 1 and 2, respectively. Structural implications are very large for 2 compared to 1 when free phosphines are replaced by chelating dppe with the P–Ni–P angle shrinking to approximately 12°. © 2003 Elsevier Ltd. All rights reserved.

Keywords: Nickel; Dithiocarbamate; PPh3; Dppe; X-ray crystal structure; NMR

## 1. Introduction

Divalent nickel complexes of dithiocarbamates with different substituents contain planar diamagnetic  $MS_4$  chromophores. Ni(II)dithiocarbamates are borderline acceptors and they prefer to react with soft Lewis bases such as phosphines and hard bases such as nitrogenous ligands [1,2]. The symbiotically induced softness and the electronic effects of the substitutents on the dithiocarbamate ligands were found to be important in deciding the reactivity [3,4]. On reaction with phosphines, they form

complexes with a NiS<sub>2</sub>P<sub>2</sub> chromophore which are again planar and diamagnetic in nature [5–7]. Synthetic and structural studies on [Ni(dtc)Cl(PPh<sub>3</sub>)] and [Ni(dtc) (PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> complexes, where dtc = S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, S<sub>2</sub>CNH(C<sub>2</sub>H<sub>4</sub>OH), S<sub>2</sub>CN(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>, S<sub>2</sub>CN(C<sub>4</sub>H<sub>8</sub>O), S<sub>2</sub>CN(C<sub>5</sub>H<sub>10</sub>) have been reported from our laboratory [8]. The effect of alkyl substitutents in the metal dithiocarbamates have been investigated earlier [9]. In order to understand the influence of free and chelating phosphines on the NiS<sub>2</sub>P<sub>2</sub> chromophore and on the thioureide C–N bond, in this paper, we report the synthesis, spectral and structural characterization of two new complexes, [Ni(dnpdtc)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> · PPh<sub>3</sub> (1), and [Ni(dnpdtc) (dppe)]BPh<sub>4</sub> (2) where, dnpdtc = *N*,*N*-dipropyldithiocarbamate.

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## 2. Experimental

All the reagents and solvents employed were commercially available analytical grade materials and were used as supplied, without further purification. IR spectra were recorded on an ABB Bomem MB 104 spectrophotometer (range 4000–400 cm<sup>-1</sup>) as KBr pellets. The UV–vis spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> on a U-2001 spectrophotometer. NMR spectra were recorded on a Bruker AMX 400 spectrometer at room temperature, using CDCl<sub>3</sub> as solvent.

## 2.1. Preparation of complexes

## 2.1.1. Bis(triphenylphosphine)(N,N-dipropyldithiocarbamato)nickel(II) perchlorate

2.1.1.1. [Ni(dnpdtc)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (1). A mixture of Ni(dnpdtc)<sub>2</sub> (210 mg, 0.5 mmo1), PPh<sub>3</sub>(520 mg, 2 mmol), NiCl<sub>2</sub> · 6H<sub>2</sub>O (120 mg, 0.5 mmol) and NH<sub>4</sub>ClO<sub>4</sub> (115 mg, 1 mmol) was refluxed for about 2 h in methanol–dichloromethane solvent mixture (50:50, 50 cm<sup>3</sup>), and was then concentrated to ca. 25 cm<sup>3</sup>. The purple-red solution obtained was filtered and was left for evaporation. The fine single crystals suitable for X-ray structural analysis were obtained by repeated recrystallization from the same solvent mixture (yield 60%, 520 mg, dec. 178 °C). Anal.

Calc. for C<sub>61</sub>H<sub>59</sub>ClNNiO<sub>4</sub>P<sub>3</sub>S<sub>2</sub>: C, 65.34; H, 5.30; N, 1.25. Found: C, 65.12; H, 5.14; N, 1.17%.

## 2.1.2. 1,2-Bis((diphenylphosphino)ethane)(N,N-dipropyldithiocarbamato)nickel(II) tetraphenylborate

2.1.2.1. [Ni(dnpdtc)(dppe)]BPh<sub>4</sub> · H<sub>2</sub>O (2). A mixture of Ni(dnpdtc)<sub>2</sub> (420 mg, 1 mmol), dppe (790 mg, 2 mmol), NiCl<sub>2</sub> · 6H<sub>2</sub>O (240 mg, 1 mmol) and NaBPh<sub>4</sub> (680 mg, 2 mmol) was refluxed for about 3 h in methanol–dichloromethane solvent mixture (50:50, 50 cm<sup>3</sup>). The solution was then concentrated to ca. 25 cm<sup>3</sup>. The purple-red solution obtained was filtered and was kept for evaporation. After 2 days a purple-red coloured solid separated out and was recrystallized from methanol–dichloromethane mixture. Single crystals suitable for X-ray structural analysis were obtained by repeated recrystallization from the same solvent mixture (yield 65%, 1.2 g, dec. 182 °C). Anal. Calc. for C<sub>57</sub>H<sub>58</sub>BNNiOP<sub>2</sub>S<sub>2</sub>: C, 70.67; H, 6.03; N, 1.44. Found: C, 70.12; H, 5.97; N, 1.32%.

#### 2.2. X-ray crystallography

Details of the crystal data, data collection and refinement parameters for 1 and 2 are summarized in Table 1. Intensity data were collected at ambient temperature (295 K) on Philips PW 100 (for 1) and SMART

Table 1

Crystal data, data collection and refinement parameters for [Ni(dnpdtc)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> and [Ni(dnpdtc)(dppe)]BPh<sub>4</sub>

Compound	[Ni(dnpdtc)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> · PPh <sub>3</sub> (1)	$[Ni(dnpdtc)(dppe)]BPh_4 \cdot H_2O$ (2)
Empirical formula	$C_{61}H_{59}CINNi_{04}P_3S_2$	$C_{57}H_{58}BNNiOP_2S_2$
Formula weight	1121.3	968.6
Colour	purple-red	purple-red
Habit	needle	column, irregular
Crystal dimensions (mm)	0.20  imes 0.29  imes 0.36	0.17  imes 0.24  imes 0.29
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	13.787 (2)	9.460 (2)
$b(\mathbf{A})$	17.625 (2)	14.526 (2)
c (Å)	12.350 (3)	21.083 (2)
α (°)	99.88 (3)	108.360 (2)
β (°)	99.09 (3)	101.370 (3)
γ (°)	74.57 (2)	90.400 (3)
$U(Å^3)$	2829.9 (9)	2688.3 (7)
Ζ	2	2
$D_{\rm c} ~({\rm g}~{\rm cm}^{-3})$	1.316	1.197
$\mu \text{ cm}^{-1} (\text{L})$	5.96	5.36
F(000)	1172	1020
$\lambda$ (Å)	Μο Κα (0.71069)	Μο Κα (0.71069)
$\theta$ range (°)	3.03-30.02	1.04-30.47
Scan type	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
Index ranges	$-19 \leq h \leq 19, -24 \leq k \leq 24, 0 \leq l \leq 15$	$-12 \leq h \leq 13, -20 \leq k \leq 14, -29 \leq l \leq 28$
Reflections collected	16150	12 357
Observed reflections $F_{\rm o} > 4\sigma(F_{\rm o})$	6791	7900
Weighting scheme	$W = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.00P]$ , where	$W = 1/[\sigma^2/(F_o^2) + (0.0968P)^2 + 0.00P]$ , where
	$P = (F_{\rm o}^2 + 2F_{\rm c}^2)/3$	$P = (F_{\rm o}^2 + 2F_{\rm c}^2)/3$
Number of parameters refined	894	836
Final $R, R_w$ (observed, data)	0.0414, 0.0890	0.0510, 0.1409
GOOF	0.816	0.904

Table 2 Bond distances (Å) and angles (°) for [Ni(dnpdtc)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> and [Ni(dnpdtc)(dppe)]BPh<sub>4</sub>

[Ni(dnpdtc)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (1)		$[Ni(dnpdtc)(dppe)]BPh_4 \cdot H_2O$ (	$[Ni(dnpdtc)(dppe)]BPh_4 \cdot H_2O$ (2)			
Bond distances						
Ni(1)–P(31)	2.1919(10)	Ni(1)–P(12)	2.1607(9)			
Ni(1)-S(3)	2.2094(9)	Ni(1)–P(15)	2.1715(7)			
Ni(1)–S(2)	2.2120(10)	Ni(1)–S(2)	2.1931(8)			
Ni(1)–P(12)	2.2253(10)	Ni(1)–S(3)	2.2108(9)			
S(2)–C(4)	1.722(3)	S(2)–C(4)	1.718(3)			
S(3)–C(4)	1.727(3)	S(3)–C(4)	1.715(3)			
C(4)–N(5)	1.304(3)	C(4)–N(5)	1.314(4)			
N(5)–C(9)	1.464(4)	N(5)–C(6)	1.477(4)			
N(5)-C(6)	1.478(3)	N(5)–C(9)	1.492(5)			
Bond angles						
P(31)–Ni(1)–S(3)	93.56(4)	P(12)–Ni(1)–P(15)	86.50(3)			
P(31)–Ni(1)–S(2)	171.99(3)	P(12)–Ni(1)–S(2)	94.72(3)			
S(3)–Ni(1)–S(2)	78.61(4)	P(15)–Ni(1)–S(2)	167.70(4)			
P(31)–Ni(1)–P(12)	98.41(4)	P(12)-Ni(1)-S(3)	172.06(3)			
S(3)–Ni(1)–P(12)	167.99(3)	P(15)–Ni(1)–S(3)	100.32(3)			
S(2)–Ni(1)–P(12)	89.45(4)	S(2)–Ni(1)–S(3)	79.49(3)			
C(4)–S(2)–Ni(1)	85.65(9)	C(4)–S(2)–Ni(1)	85.25(10)			
C(4)–S(3)–Ni(1)	85.60(9)	C(4)–S(3)–Ni(1)	84.74(10)			
N(5)-C(4)-S(2)	124.8(2)	N(5)–C(4)–S(3)	125.3(2)			
N(5)-C(4)-S(3)	126.6(2)	N(5)–C(4)–S(2)	124.4(2)			
S(2)-C(4)-S(3)	108.60(14)	S(3)–C(4)–S(2)	110.21(16)			
C(4)–N(5)–C(9)	120.7(2)	C(4)–N(5)–C(6)	122.7(3)			
C(4)–N(5)–C(6)	121.9(3)	C(4)–N(5)–C(9)	120.9(3)			
C(9)–N(5)–C(6)	117.3(2)	C(6)-N(5)-C(9)	116.1(3)			
N(5)-C(6)-C(7)	111.7(3)	N(5)-C(6)-C(7)	111.8(3)			

AXS (for 2) diffractometers using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). Lorentz and polarization corrections were applied. The structures were solved by direct methods using SHELXS-97 [10] and were refined by SHELXL-97 [11]. 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 2.

#### 3. Results and discussion

#### 3.1. IR spectral studies

The IR spectrum of **1** shows the thioureide  $v_{C-N}$  band at 1536 cm<sup>-1</sup> and that of compound **2** at 1526 cm<sup>-1</sup>. The mesomeric shift of electrons from the dithiocarbamate

Table 3 NMR spectral data (chemical shift values in ppm)

moiety towards the metal centre increases the contribution of the polar thioureide form in both the cases. This is reflected in the shift in  $v_{C-N}$  values to higher wave numbers compared with that observed in the parent complex at 1508 cm<sup>-1</sup>. The  $v_{C-S}$  band appears at 1091 cm<sup>-1</sup> for **1** and 999 cm<sup>-1</sup> for **2** without any splitting, supporting the bidentate coordination of the dithiocarbamate moiety [12].

#### 3.2. NMR spectral studies

NMR spectra were recorded at room temperature using TMS as an internal reference. For all the compounds CDCl<sub>3</sub> was used as solvent. The <sup>13</sup>C NMR spectra were recorded in the proton decoupled mode. The <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR chemical shift values are given in Table 3 with splitting patterns.

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Compound	NMR	$PPh_x$	$BPh_4$	$CH_3$	$\beta$ -CH <sub>2</sub>	$\alpha$ -CH <sub>2</sub>	$-PCH_2CH_2P-$	$S_2^{13}CN$		
1	<sup>1</sup> H <sup>13</sup> C <sup>31</sup> P	7.20–7.60(m) 128–137 31.0		0.81(t) 11.06	1.61(m) 20.70	3.50(t) 51.13		199.17		
2	<sup>1</sup> H <sup>13</sup> C <sup>31</sup> P	7.10–7.60(m) 121–136	6.7–6.9 163–165	0.88(t) 11.12	1.62(m) 20.71	3.49(t) 51.27	1.91(t) 25.80 60.80	201.88		

Where x = 3 for compound 1 and 2 for compound 2.

## 3.2.1. <sup>1</sup>H NMR

For compound 1, the methyl group protons resonate at 0.81 ppm as a triplet. The methylene protons were observed at 1.61 and 3.50 ppm. Of these two signals, the triplet at 3.50 ppm was assigned to  $\alpha$ -CH<sub>2</sub> protons and the multiplet at 1.61 ppm was assigned to  $\beta$ -CH<sub>2</sub> protons. A multiplet in the region of 7.20–7.60 ppm was due to aromatic protons. For compound **2**, apart from the propyl group signals (the splitting pattern was the same as observed for compound **1**), a triplet in the upfield region of 1.91 ppm was assigned to methylene protons present in the chelating phosphine. In the downfield region, two sets of signals were obtained for aromatic protons of PPh<sub>3</sub> and BPh<sub>4</sub>.

## 3.2.2. <sup>13</sup>C NMR

The chemical shifts of thioureide carbon  $(N^{-13}CS_2)$ were observed at 199.17 and 201.88 ppm for complexes **1** and **2**, respectively. The slight upfield shift from the normal chemical shift values of Ni(dtc)<sub>2</sub> complexes (206–210 ppm) [13] is supported by the higher  $v_{C-N}$ values observed for complexes **1** and **2** in the present study. This was due to the mesomeric shift of electron density from the dithiocarbamate moiety towards the metal centre. This supports the bidentate coordination of the dithiocarbamate and the strong back bonding in both the compounds. For compound **2**, the low intensity signals in the region of 163–165 ppm were due to BPh<sub>4</sub> aromatic carbons.

## 3.2.3. <sup>31</sup>P NMR

<sup>31</sup>P NMR for compound **1** shows a signal at 31 ppm and is assigned to coordinated phosphorus. The free PPh<sub>3</sub> phosphorus resonates at the more upfield region of -5.8 ppm. For compound **2**, the signal at 60.8 ppm is assigned to the phosphorus of the chelating phosphine [14]. The very high deshielding for the coordinated phosphorus in both the cases compared with the free phosphines indicates the drift of electron density from the phosphorus towards the metal centre. The shift is phenomenal with the free dppe chemical shift being observed at 40 ppm [15].

#### 3.3. BVS calculations

For the two complexes, BVS values were calculated by two procedures [16,17]. The values are 3.0646 (B/ OK), 2.9338 (OK/B); 3.2629 (B/OK), 3.1602 (OK/B) for the two complexes **1** and **2**, respectively. In 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 [18].

### 3.4. Structural analysis

The ORTEP diagram of 1 is shown in Fig. 1. Two units of  $[Ni(dnpdtc)(PPh_3)_2]ClO_4 \cdot PPh_3$  are present in the unit cell. It is interesting to note that a free triphenylphosphine molecule is also present along with the complex in the unit cell. The NiS<sub>2</sub>P<sub>2</sub> chromophore is not of perfect square planar geometry because of the small bite angle associated with the dithiocarbamate moiety [78.61(4)°]. The Ni-P distances [2.1919(10) and 2.2253(10) Å] show asymmetry, as reported earlier for similar compounds [8]. The planarity of the molecule is in keeping with the observed diamagnetism of the complex. The asymmetry in the Ni-P distances and the observed large P-Ni-P bond angle is due to the bulkiness of the PPh3 group. The C-S bond lengths are 1.722(3) and 1.727(4) Å, which are shorter than the single bond length of 1.81 Å and higher than the C=S distance of 1.69 Å. The observed intermediate value between the single and double bond distances indicates a partial double bond character. The short thioureide C-N distance, 1.304(3) A, indicates that the  $\pi$  electron density is delocalized over the S<sub>2</sub>CN moiety and that this bond has a strong double bond character. This is also confirmed by the fact that the two S-C-N angles are much greater than that of the S–C–S  $(108.60(14)^{\circ})$  angle.

There is a shortening of the Ni–P distances for the N,N-dipropyl analogue [2.1919(10) and 2.2253(10) Å] compared to its N,N-diisopropyl analogue [2.215(2) and 2.224(3) Å] [19]. Also, the S–Ni–S angle decreases in the N,N-diisopropyl compound [77.7(1) Å] compared to that in the N,N-dipropyldithiocarbamate analogue [78.61(4) Å] indicating a reduced steric requirement of the isopropyl compound. In [Ni(dnpdtc)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>



Fig. 1. ORTEP diagram for compound 1 (PPh<sub>3</sub> is omitted for clarity).

(1) the thioureide C–N distance is 1.304(3) Å and in  $[Ni(dipdtc)(PPh_3)_2]ClO_4$  it is 1.321(11) Å, the observed reduction of the thioureide distance in 1 shows the effective  $\pi$  back bonding of the phosphines in 1. The Cl–O distances vary from 1.340 to 1.421 Å and the O–Cl–O angles vary from 107.8° to 112.5° in 1 indicating the distortion from tetrahedral geometry. The phenyl rings show normal bond parameters. The P–C bond distances are also normal with an average value of 1.8286 Å. The C–P–C angles deviate appreciably from the ideal tetrahedral angle of 109.5° and the resultant crowding of the phenyl rings causes the P–C–C angles to be asymmetric.

[Ni(dnpdtc)(dppe)]BPh<sub>4</sub> (2) is monomeric with two molecules per unit cell. The ORTEP diagram of the molecule is shown in Fig. 2. The molecule is approximately planar, in keeping with the observed diamagnetism. The Ni-S [2.1931(8) and 2.2108(9) Å] and C-S [1.718(3) and 1.715(3) A] bonds are symmetric, showing that the negative charge on the dithiocarbamate ligand is equally distributed all over the two donor atoms as found in 1. One molecule of water is found in the unit cell. The short thioureide C-N distance of 1.314(4) A indicates that the electron density is delocalized over the  $S_2CN$  moiety and this bond has partial double bond character. The bond lengths and bond angles of [Ni(dipdtc)(dppe)]<sup>+</sup> reported from our laboratory [19] show a similarity in thioureide C–N distance [(1.314(4))]A] in 2, and 1.316(8) A in  $[Ni(dipdtc)(dppe)]^+$ ). The N,N-dipropyl complexes (1) and (2) exhibit a relatively larger steric influence compared to the diisopropyl analogue. In 2, the P-Ni-P angle is 86.50(3)° which



Fig. 2. ORTEP diagram for compound 2 (BPh<sub>4</sub> and H<sub>2</sub>O are omitted for clarity).

is smaller than that in the diisopropyl analogue:  $87.3(1)^{\circ}$ .

Comparison of 1 and 2 shows that S-Ni-S bite angles [78.61(4)° versus 79.49(3)°] and the Ni-S-C angles [85.625° versus 84.995°] are very similar. On the other hand, a significant difference is observed in the P-Ni-P angles that are subtended by dppe, a bidentate ligand, being about 12° smaller than that found in 1, where the PPh<sub>3</sub> groups exert higher steric hindrance. Thus, the P-Ni-P angles show a large change and are influenced by the bulkiness of the nature of the phosphines. The thioureide C-N bond is 1 is shorter than the bond in 2. The significant shortening is a clear manifestation of mesomeric shift of electron density towards nickel through the thioureide C-N bond in 1 compared to 2. Though the Ni-P bonds in 2 are relatively shorter than those in 1, the back bonding effects are felt more pronounced in 1 and hence the corresponding thioureide bond shows a shortening of its length. As a result of the reduced P-Ni-P chelated angle in 2, the S-Ni-S angle increases by 0.49° compared to 1. Hence, both electronic and steric influences of dppe over PPh<sub>3</sub> are exemplified by compound 2 with respect to the compound 1.

#### 4. Supplementary data

Supplementary data are available from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk) on request, quoting the deposition number(s) CCDC 211258 and CCDC 211259.

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