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Polyhedron 22 (2003) 1341–1348



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# O,O'-Dialkyldithiophosphato and O-alkyldithiophosphato nickel(II) complexes with bidentate P-donor ligands

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Received 26 November 2002; accepted 10 February 2003

## Abstract

The following complexes, having the general formula  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OR})(\text{P}-\text{P})]$   $\{\text{R} = \text{Et}$  (1), *i*-Pr (2), P–P = dppe; R = Et (3), P–P = 1,4-bis(diphenylphosphino)butane (dppb)},  $[\text{Ni}(\text{S}_2\text{P}\{\text{OR}\}_2)(\text{P}-\text{P})\text{X}]$   $\{\text{R} = i\text{-Pr}$  (4), Et (5), P–P = 1,2-bis(diphenylphosphino)ethane (dppe); R = Et, P–P = 1,1-bis(diphenylphosphino)methane (dppm) (6); X =  $\text{ClO}_4^-$  } and  $[\text{Ni}(\text{S}_2\text{P}\{\text{OR}\}_2)(\text{dppe})\text{X}]$   $\{\text{R} = i\text{-Pr}$ , X =  $\text{NCS}^-$  (7); R = Et, X =  $\text{Br}^-$  (8)}, have been synthesized. All the compounds have been characterized by elemental analyses, IR, UV–Vis, and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectral studies, magnetic and conductivity measurements. Single crystal X-ray analysis revealed the molecular structures of  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})(\text{dppe})]$  (1),  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})(\text{dppb})]\cdot\text{EtOH}$  (3) and  $[\text{Ni}(\text{S}_2\text{P}\{\text{OEt}\}_2)(\text{dppe})]\text{ClO}_4$  (5), and confirmed a square-planar geometry around the nickel atoms. We have reason to believe that the coordination geometry in  $[\text{Ni}(\text{S}_2\text{P}\{\text{OEt}\}_2)(\text{dppe})\text{Br}]\cdot\text{H}_2\text{O}$  (8) is probably tetrahedral with monodentate coordinated  $(\text{S}_2\text{P}\{\text{OEt}\}_2)$  monoanion.

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**Keywords:** Nickel(II); Dithiophosphates; Syntheses; X-ray structures

## 1. Introduction

O,O'-Dialkyl(aryl)esters of dithiophosphoric acid  $(\text{RO})_2\text{P}(\text{S})\text{SH}$  have been well documented [1], with previous applications as insecticides and as inhibitors of hydrolysis of the enzyme acetylcholinesterase to its substrate acetylcholine, thus causing muscular paralysis [2]. The insecticidal, rodenticidal and fungicidal activities of esters with the general formula  $(\text{RO})_2\text{P}(\text{S})\text{SX}$  (X = acetylphenyl or alkylurea), as well as the use of these compounds in the process of rubber vulcanization have also been described [3,4]. O,O'-Dialkyldithiophosphates can also be used in analytical chemistry as extraction agents [5], such as the proposed use of bis(O,O'-dipropyldithiophosphato)nickel(II) for spectroscopic determination of the alcohol contents in alcoholic drinks [6]. In relation to these findings, square-planar complexes with the formula  $[\text{Ni}(\text{S}_2\text{P}\{\text{OR}\}_2)]$  have been also investigated for several

decades [7]. These complexes, with the ligands acting as a chelate and forming four-membered rings with nickel, can readily react with both monodentate and polydentate nitrogen- or phosphorus-donor ligands, thereby increasing the coordination number of nickel.

To date, considerable attention has been devoted to adducts of  $[\text{Ni}(\text{S}_2\text{P}\{\text{OR}\}_2)_2]$  with nitrogen-donor ligands [3,8–10]. Only a few studies have focused on the preparation and characterization of nickel-dithiophosphato complexes in combination with monodentate P-donor ligands [11–14], especially with those that are of a bidentate nature [15]. However, the reaction between  $[\text{Ni}(\text{S}_2\text{P}\{\text{OMe}\}_2)_2]$  and dppe (dppe =  $\text{Ph}_2\text{P}-\text{CH}_2\text{CH}_2-\text{PPh}_2$ ) led to formation of  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OMe})(\text{dppe})]$ . Thus, the reaction is accompanied by the removal of one  $(\text{S}_2\text{P}\{\text{OMe}\}_2)^-$  ligand and the elimination of a methyl group from the other  $(\text{S}_2\text{P}\{\text{OMe}\}_2)^-$  to afford  $(\text{S}_2\text{P}\{\text{O}\}\text{OMe})^{2-}$ . In the case of  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OR})(\text{dpae})]\cdot 0.5\text{C}_6\text{H}_6$ , where (dpae =  $\text{Ph}_2\text{P}-\text{CH}_2\text{CH}_2-\text{AsPh}_2$ ), single crystal X-ray analysis confirmed the existence of the derived product [15]. A similar elimination has been also observed in  $[\text{Pd}(\text{PPh}_3)_2(\text{S}_2\text{P}\{\text{O}\}i\text{-Pr})]$  for which the X-ray structure has been determined [16].

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Here, we describe the preparation and characterization of the new nickel(II) mixed ligand complexes containing bidentate phosphorus donor ligands (dppm, dppe, dppb) and  $(S_2P\{OR\}_2)^-$  [O,O'-dialkyldithiophosphates] or  $(S_2P\{O\}OR)^{2-}$  [O-alkyldithiophosphates] in the coordination sphere of nickel but also the first examples of their X-ray structural characterizations.

## 2. Experimental

### 2.1. Materials

$P_4S_{10}$ , dppm, dppe and dppb were obtained commercially from Fluka or Aldrich.  $Ni(ClO_4)_2 \cdot 6H_2O$  and  $Ni(SCN)_2 \cdot 2H_2O$  were purchased from Lachema and used without further purification.  $[Ni(S_2P\{OEt\}_2)_2]$  and  $[Ni(S_2P\{O-i-Pr\}_2)_2]$  were prepared by the methods reported in Ref. [3].

### 2.2. Syntheses of nickel(II) complexes

#### 2.2.1. $[Ni(S_2P\{O\}OEt)(dppe)]$ (1), $[Ni(S_2P\{O\}O-i-Pr)(dppe)]$ (2) and $[Ni(S_2P\{O\}OEt)(dppb)] \cdot EtOH$ (3)

Dppe (1 mmol) was added to an EtOH solution (40  $cm^3$ ) of  $[Ni(S_2P\{OEt\}_2)_2]$  (1 mmol). The mixture was stirred under reflux for 4 h. The solution was then filtered and kept at low temperature ( $\approx 4^\circ C$ ) for 10 days. The orange crystalline solid, formed, was separated, washed with petroleum ether and finally dried in a vacuum desiccator. The crystals obtained were suitable for X-ray diffraction study. Compounds 2 and 3 were prepared by the same method, the appropriate ligands were used only.

#### 2.2.2. $[Ni(S_2P\{O-i-Pr\}_2)(dppe)]ClO_4$ (4)

Finely powdered  $[Ni(S_2P\{O-i-Pr\}_2)_2]$  (1 mmol) was added to a suspension of  $Ni(ClO_4)_2 \cdot 6H_2O$  (1 mmol) in  $CHCl_3$  (40  $cm^3$ ), then stirred at room temperature. To the resulting mixture, dppe (1 mmol) was added. The solution immediately turned to an orange–brown colour. The solution was heated under reflux and stirred for 4 h, then filtered. Approximately 4/5 of the original volume was allowed to evaporate at room temperature. An excess of  $Et_2O$  was then added into the mixture. Yellow microcrystals were obtained by this procedure, which were filtered, washed with  $Et_2O$  and dried in a vacuum desiccator.

#### 2.2.3. $[Ni(S_2P\{OEt\}_2)_2(dppe)]ClO_4$ (5)

The complex was prepared by the similar procedure as described above for  $[Ni(S_2P\{O-i-Pr\}_2)(dppe)]ClO_4$  (4), except  $[Ni(S_2P\{OEt\}_2)_2]$  (1 mmol) was used instead of  $[Ni(S_2P\{O-i-Pr\}_2)_2]$  and an abs. EtOH was used as the solvent. Yellow needles, which were obtained by

slowly evaporating the solvent at  $4^\circ C$ , were suitable for X-ray diffraction study.

#### 2.2.4. $[Ni(S_2P\{OEt\}_2)(dppm)]ClO_4 \cdot H_2O$ (6), $[Ni(S_2P\{O-i-Pr\}_2)(dppe)(NCS)]$ (7) and $[Ni(S_2P\{OEt\}_2)(dppe)Br] \cdot H_2O$ (8)

The complex  $[Ni(S_2P\{OEt\}_2)(dppm)]ClO_4 \cdot H_2O$  (6) was obtained as a light orange crystalline product using the similar procedure as described for compound 5, while the complexes  $[Ni(S_2P\{O-i-Pr\}_2)(dppe)(NCS)]$  (7) and  $[Ni(S_2P\{OEt\}_2)(dppe)Br] \cdot H_2O$  (8) were prepared by the same method as for 4. Unfortunately, the crystals of these products were unsuitable for single crystal X-ray analysis.

### 2.3. Methods

Partial elemental analyses (C, H, N) were performed on an EA1108 CHN analyser (Fisons Instruments). The chlorine and bromine contents were determined by the Schöniger's method, while the nickel content was estimated by chelatometric titration. Electronic absorption spectra (diffuse-reflectance) were obtained with a SPECORD M40 (Carl Zeiss, Jena) spectrometer within the 11 000–35 000  $cm^{-1}$  range. Far-IR spectra were carried out on a FT-IR NEXUS 670 spectrometer (Thermo Nicolet) in the region of 150–600  $cm^{-1}$ . Mid-IR spectra were obtained with a Specord M80 instrument (Carl Zeiss, Jena) in the 400–4000  $cm^{-1}$  region. Molar conductivities were performed using a Cond340i/SET Conductivity Meter (WTW, Germany) in DMFA and acetone at  $25^\circ C$ . The concentration of the complexes in solutions was  $10^{-3}$  mol  $dm^{-3}$ .

Magnetic susceptibilities of all the complexes were measured by the Faraday method at 298 K.  $Hg[Co(NCS)_4]$  was used as a calibrant. In the case of complex 8, data were corrected for diamagnetic contributions using Pascal's constants [17].  $^{31}P\{^1H\}$  NMR spectra were measured on a Bruker Avance DRX 300 spectrometer operating at frequencies of 121.44 MHz ( $^{31}P$ ). The measurements were performed at 300 K. The samples were prepared by dissolving the compounds in  $CDCl_3$ , and 85%  $H_3PO_4$  was used as an external reference.

### 2.4. X-ray structure determinations

Diffraction experiments for the complexes  $[Ni(S_2P\{O\}OEt)(dppe)]$  (1),  $[Ni(S_2P\{O\}OEt)(dppb)] \cdot EtOH$  (3) and  $[Ni(S_2P\{OEt\}_2)(dppe)]ClO_4$  (5) were carried out on a four circle  $\kappa$ -axis KUMA KM-4 diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at 120(2) K. Data collections for the complexes 1, 3 and 5 were performed using a CCD detector (KUMA Diffraction, Wrocław). KUMA KM4RED software was used for data reduction. All the

structures were solved by using the SIR-97 program [18] incorporated in the WinGX system [19]. All non-hydrogen atoms of **1**, **3** and **5** were refined anisotropically by the full-matrix least-squares procedure (SHELXL-97) [20] with weights:  $w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.7829P]$  for **1**,  $w = 1/[\sigma^2(F_o^2) + (0.0375P)^2]$  for **3** and  $w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 3.8187P]$  for **5**, where  $P = (F_o^2 + 2F_c^2)/3$ . All H-atom positions in **1** and **5** were located from Fourier difference maps and all their parameters were refined, except for H-atoms in **3** bonded to C(1), C(2) and C(4) which were positioned theoretically to idealized positions and treated using a combination of riding, rigid and/or rotating model (AFIX 23, AFIX 137). The remaining H-atoms in **3** were found in the Fourier difference maps. Their parameters were refined isotropically. Hydrogen atom associated with EtOH in **3** was not found in the difference maps and so is not included in the model. The C(31) atom as well as the hydrogens bonded to it of EtOH are disordered over two positions. The remaining H-atoms belonging to C(32) in EtOH were refined using a combination of the rigid and rotating models (AFIX 137).

The largest peak and hole on the final difference map for **1**, **3** and **5** were 0.415 [1.00 Å from P(1)] and  $-0.300$  [0.80 Å from P(1)]  $e \text{ \AA}^{-3}$ , 0.460 [1.00 Å from C(29)] and  $-0.334$  [0.77 Å from P(1)]  $e \text{ \AA}^{-3}$ , and 1.031 [1.07 Å from C(1)] and  $-0.403$  [0.44 Å from C(4)]  $e \text{ \AA}^{-3}$ , respectively. Additional crystallographic details are given in Table 1.

### 3. Results and discussion

#### 3.1. General features

Chemical compositions, colours, magnetic susceptibilities and molar conductivity values of the Ni<sup>II</sup> complexes are included in Table 2. All of the prepared complexes are stable on air, soluble in DMFA, acetone and EtOH, and insoluble in *n*-hexane and Et<sub>2</sub>O. The reaction between [Ni(S<sub>2</sub>P{OR}<sub>2</sub>)<sub>2</sub>] (R = Et, *i*-Pr) and bidentate P–P ligand (dppe or dppb) in EtOH (molar ratio 1:1) gave complexes of the composition [Ni(S<sub>2</sub>P{O}OR)(P–P)] (**1–3**). By the reaction of the bidentate phosphorus ligand (P–P) with [Ni(S<sub>2</sub>P{OR}<sub>2</sub>)<sub>2</sub>] and NiX<sub>2</sub>·*n*H<sub>2</sub>O (X = ClO<sub>4</sub><sup>−</sup>, Br<sup>−</sup>, NCS<sup>−</sup>), two following types of complexes were obtained: [Ni(S<sub>2</sub>P{OR}<sub>2</sub>)(P–P)]X (X = ClO<sub>4</sub><sup>−</sup>) (**4–6**) and [Ni(S<sub>2</sub>P{OR}<sub>2</sub>)(P–P)]X {X = NCS<sup>−</sup> (**7**), Br<sup>−</sup> (**8**)}. To our knowledge, these last two types of nickel(II) complexes with these specific combination of ligands have not yet been prepared. To date, neither has any reference to these types of nickel(II) complexes been found in the Cambridge Crystallographic Data Centre [21]. A mechanism for elimination of the methyl group

for [Ni(S<sub>2</sub>P{O}OR)(P–P)] was already observed and suggested by Gastaldi et al. [15]. The IR, electronic and <sup>31</sup>P{<sup>1</sup>H} NMR spectral data of the prepared complexes are summarized in Table 3.

#### 3.2. Conductivity and magnetic data

From molar conductivity values presented in Table 2 is clearly apparent that complexes **4–6** behave as 1:1 electrolytes in DMFA and acetone solutions [22]. The results show that perchlorate anions in these complexes are situated outside of the inner coordination sphere of the central atom. The molar conductivities found for all the remaining complexes [**1–3**, **7** and **8**] illustrate the non-ionic features of these compounds in the solvents used. Somewhat higher λ<sub>M</sub> values in DMFA established for **7** and **8** can be connected with possible partial dissociation of the compounds in this solvent. The complexes **1–7** are diamagnetic (see Table 2), while complex **8** is paramagnetic with a room temperature magnetic moment of 3.22 μ<sub>eff</sub>/μ<sub>B</sub>, indicating that the central nickel(II) atom is in the high-spin state containing two unpaired electrons [23]. Based on conductivity and magnetic data and taking into account results from <sup>31</sup>P{<sup>1</sup>H} NMR and IR spectral data (see below), we assume a tetrahedral geometry in [Ni(S<sub>2</sub>P{OEt}<sub>2</sub>)<sub>2</sub>-(dppe)Br]·H<sub>2</sub>O (**8**) with [S<sub>2</sub>P{OEt}<sub>2</sub>]<sup>−</sup> acting probably as a monodentate ligand. Although, owing to the lack of an X-ray structure, it is not possible to make a final decision about coordination geometry around nickel in the latter complex at this point. We suggest a square-planar geometry around nickel in all the remaining complexes **1–7**.

#### 3.3. P{<sup>1</sup>H} NMR spectra

A comparison to observed resonances found for free and coordinated S<sub>2</sub>P{OR}<sub>2</sub> and S<sub>2</sub>P{O}OR anions, and P–P ligands in transition metal coordination compounds can be used for the interpretation of <sup>31</sup>P{<sup>1</sup>H} NMR spectra of our nickel(II) complexes. Resonances due to free dppe, dppe and dppb ligands are observed in CDCl<sub>3</sub> at δ  $-22.34$ ,  $-12.45$ , and  $-15.98$  ppm, respectively. A signal at approximately δ 133 ppm in CD<sub>2</sub>Cl<sub>2</sub> is produced by free [S<sub>2</sub>P{OR}<sub>2</sub>]<sup>−</sup> [24]. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **1–3** measured in CDCl<sub>3</sub> solutions gave peaks at δ 56.70–61.84 ppm indicating probably the bidentate nature of the S<sub>2</sub>P{O}OR dianion in the nickel complexes. The resonances observed at δ 57.41 ppm for **1**, 56.66 ppm for **2** and 28.49 ppm for **3** can be connected with bidentate coordination of the corresponding P–P ligand. This assertion can be further supported by observing the resonances which are belonging to these ligands appear at 62.80 ppm and 30.0 ppm for [Ni(dppe)(pipdte)](ClO<sub>4</sub>), and [Ni(dppb)(pipdte)](ClO<sub>4</sub>) {pipdte = piperidinedithiocar-

Table 1

Crystal data and structure refinement for [Ni(S<sub>2</sub>P{O}OEt)(dppe)] (1), [Ni(S<sub>2</sub>P{O}OEt)(dppb)]·EtOH (3) and [Ni(S<sub>2</sub>P{OEt}<sub>2</sub>)(dppe)]ClO<sub>4</sub> (5)

Compound	1	3	5
Empirical formula	C <sub>28</sub> H <sub>29</sub> NiO <sub>2</sub> P <sub>3</sub> S <sub>2</sub>	C <sub>32</sub> H <sub>38</sub> NiO <sub>3</sub> P <sub>3</sub> S <sub>2</sub>	C <sub>30</sub> H <sub>34</sub> ClNiO <sub>6</sub> P <sub>3</sub> S <sub>2</sub>
Formula weight	613.25	686.36	741.76
Temperature (K)	120(2)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	9.6064(6)	10.4475(4)	9.3052(4)
<i>b</i> (Å)	17.2244(13)	18.1261(8)	17.6954(7)
<i>c</i> (Å)	16.6954(10)	17.0028(8)	21.0597(9)
$\alpha$ (°)	90	90	90
$\beta$ (°)	90.291(6)	93.982(4)	101.591(4)
$\gamma$ (°)	90	90	90
Volume (Å <sup>3</sup> )	2762.5(3)	3212.1(2)	3397.0(2)
<i>Z</i>	4	4	4
<i>D</i> <sub>Calc</sub> (g cm <sup>-3</sup> )	1.475	1.419	1.450
Absorption coefficient (mm <sup>-1</sup> )	1.053	0.916	0.954
<i>F</i> (0 0 0)	1272	1436	1536
Crystal size (mm)	0.50 × 0.50 × 0.30	0.50 × 0.50 × 0.40	0.60 × 0.30 × 0.20
$\theta$ Range for data collection (°)	3.40 to 28.52	3.20 to 25.00	3.46 to 25.00
Index ranges ( <i>h</i> , <i>k</i> , <i>l</i> )	-12 ≤ <i>h</i> ≤ 12 -22 ≤ <i>k</i> ≤ 21 -20 ≤ <i>l</i> ≤ 22	-8 ≤ <i>h</i> ≤ 12 -21 ≤ <i>k</i> ≤ 21 -20 ≤ <i>l</i> ≤ 20	-11 ≤ <i>h</i> ≤ 11 -19 ≤ <i>k</i> ≤ 21 -21 ≤ <i>l</i> ≤ 25
Reflections collected	17 550	16 453	18 024
Independent reflections	6490 [ <i>R</i> <sub>int</sub> = 0.0440]	5614 [ <i>R</i> <sub>int</sub> = 0.0364]	5946 [ <i>R</i> <sub>int</sub> = 0.0341]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>		
Data/restraints/parameters	6490/0/441	5614/0/530	5946/0/494
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.987	1.012	1.011
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0360, <i>wR</i> <sub>2</sub> = 0.0743	<i>R</i> <sub>1</sub> = 0.0302, <i>wR</i> <sub>2</sub> = 0.0679	<i>R</i> <sub>1</sub> = 0.0314, <i>wR</i> <sub>2</sub> = 0.0741
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0550, <i>wR</i> <sub>2</sub> = 0.0812	<i>R</i> <sub>1</sub> = 0.0438, <i>wR</i> <sub>2</sub> = 0.0729	<i>R</i> <sub>1</sub> = 0.0369, <i>wR</i> <sub>2</sub> = 0.0767

Table 2

Colours, chemical compositions, magnetic data and molar conductivities of the complexes 1–8

Compound	Colour	Found (Calc.) (%)				$\mu_{\text{eff}}/\mu_{\text{B}}$	$\lambda_{\text{M}}$ (S cm <sup>2</sup> mol <sup>-1</sup> )
		Ni	C	H	X		
[Ni(S <sub>2</sub> P{O}OEt)(dppe)] (1)	orange	9.6 (9.6)	54.9 (54.8)	4.9 (4.8)	—	Dia	1.2 <sup>a</sup> 3.2 <sup>b</sup>
[Ni(S <sub>2</sub> P{O}O- <i>i</i> -Pr)(dppe)] (2)	orange	9.7 (9.4)	55.9 (55.5)	5.2 (5.0)	—	Dia	0.8 <sup>a</sup> 1.5 <sup>b</sup>
[Ni(S <sub>2</sub> P{O}OEt)(dppb)]·EtOH (3)	light red	8.6 (8.5)	56.0 (55.9)	5.6 (5.7)	—	Dia	1.1 <sup>a</sup> 1.2 <sup>b</sup>
[Ni(S <sub>2</sub> P{O- <i>i</i> -Pr} <sub>2</sub> )(dppe)]ClO <sub>4</sub> (4)	yellow	7.2 (7.6)	49.3 (49.9)	5.0 (5.0)	4.6 (4.6)	Dia	70.0 <sup>a</sup> 105.8 <sup>b</sup>
[Ni(S <sub>2</sub> P{OEt} <sub>2</sub> )(dppe)]ClO <sub>4</sub> (5)	yellow	7.9 (7.9)	48.5 (48.6)	4.7 (4.6)	4.7 (4.8)	Dia	69.4 <sup>a</sup> 120.2 <sup>b</sup>
[Ni(S <sub>2</sub> P{OEt} <sub>2</sub> )(dppm)]ClO <sub>4</sub> ·H <sub>2</sub> O (6)	light orange	7.9 (7.9)	46.9 (46.7)	4.4 (4.6)	4.7 (4.8)	Dia	95.0 <sup>a</sup> 140.2 <sup>b</sup>
[Ni(S <sub>2</sub> P{O- <i>i</i> -Pr} <sub>2</sub> )(dppe)(NCS)] (7)	yellow	8.4 (8.1)	54.9 (54.4)	5.0 (5.3)	1.8 (1.9)	Dia	44.6 <sup>a</sup> 11.5 <sup>b</sup>
[Ni(S <sub>2</sub> P{OEt} <sub>2</sub> )(dppe)Br]·H <sub>2</sub> O (8)	light brown	7.6 (7.9)	48.8 (48.7)	4.5 (4.9)	10.8 (10.8)	3.22	34.5 <sup>a</sup> 11.7 <sup>b</sup>

X = Cl, Br or N; Dia = diamagnetic.

<sup>a</sup> Measured in DMFA.<sup>b</sup> Measured in acetone.

Table 3  
IR, diffuse-reflectance and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectral data of the complexes **1–8**

Compound	IR [ $\text{cm}^{-1}$ ]				VIS $\times 10^3$ [ $\text{cm}^{-1}$ ] <sup>a</sup>	$^{31}\text{P}\{^1\text{H}\}$ NMR	
	$\nu(\text{Ni-S})$	$\nu(\text{P-S})_s$	$\nu(\text{P-S})_{as}$	$\nu(\text{P-O})$		P–P <sup>b</sup>	dtp <sup>c</sup>
[Ni(S <sub>2</sub> P{O}OEt)(dppe)] ( <b>1</b> )	333s 359s	533vs	660m	996s 1042s	19.5 26.0	57.41(s)	61.84(s)
[Ni(S <sub>2</sub> P{O}O- <i>i</i> -Pr)(dppe)] ( <b>2</b> )	345s	532vs	660m	996s 1042s	19.4 26.0	56.66(s)	60.94(s)
[Ni(S <sub>2</sub> P{O}OEt)(dppb)]·EtOH ( <b>3</b> )	340m 363m	525vs	659m	998m 1046s	19.0 26.0	28.49(s)	56.70(s)
[Ni(S <sub>2</sub> P{O- <i>i</i> -Pr} <sub>2</sub> )(dppe)]ClO <sub>4</sub> ( <b>4</b> )	331m 363w	529vs	656s	984s 1046w	26.0	66.30(s)	84.76(s)
[Ni(S <sub>2</sub> P{OEt} <sub>2</sub> )(dppe)]ClO <sub>4</sub> ( <b>5</b> )	331s 355m	528vs	660s	988s 1042s	26.1	66.34(s)	89.22(s)
[Ni(S <sub>2</sub> P{OEt} <sub>2</sub> )(dppm)]ClO <sub>4</sub> ·H <sub>2</sub> O ( <b>6</b> )	330s 357m	536s	654m	988s	26.0	-33.64(s)	88.92(s)
[Ni(S <sub>2</sub> P{O- <i>i</i> -Pr} <sub>2</sub> )(dppe)(NCS)] ( <b>7</b> )	331s	534vs	689vs <sup>d</sup>	998s 1044s	26.0	61.13(s)	55.56(s)
[Ni(S <sub>2</sub> P{OEt} <sub>2</sub> )(dppe)Br]·H <sub>2</sub> O ( <b>8</b> )	348w 360w	531vs	692vs <sup>d</sup>	998m 1044s	14.0 25.0	61.97(br)	57.37(br)

<sup>a</sup> Diffuse reflectance.

<sup>b</sup> P–P = dppm, dppe or dppb.

<sup>c</sup> dtp = Dithiophosphate anion; br = broad signal.

<sup>d</sup>  $\nu(\text{P=S})$ .

bamate anion}, respectively [25]. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the complexes **4–6** containing ionic perchlorate anion show resonances at 84.76, 89.22 and 88.92 ppm, respectively, due to bidentate nature of S<sub>2</sub>P{OR}<sub>2</sub> monoanion. This deduction can be made owing to the fact that peaks observed at 92.80 and 89.47 ppm in  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of [Ni(S<sub>2</sub>P{OEt}<sub>2</sub>)<sub>2</sub>], and [Ni(S<sub>2</sub>P{O-*i*-Pr}<sub>2</sub>)<sub>2</sub>], respectively, correspond to bidentate chelated S<sub>2</sub>P{OR}<sub>2</sub> monoanions to nickel. This is also consistent with literature data (92.9 ppm) found for  $^{31}\text{P}$  NMR spectrum of [Ni(S<sub>2</sub>P{OEt}<sub>2</sub>)<sub>2</sub>] measured in CDCl<sub>3</sub> [26]. The bidentate nature of P–P ligands in **4–8** can be supported by chemical shifts observed at 66.30 ppm for dppe in **4**, 66.34 ppm for dppe in **5**, -33.64 ppm for dppm in **6**, 61.13 ppm for dppe in **7** and 61.97 ppm for dppe in **8** [25]. The assignment of the peak at -33.64 ppm to bidentate coordination of dppm in **6** is also consistent with the assignment for [ $\eta^1$ -dppm)-( $\eta^2$ -dppm)Pt( $\eta^1$ -S<sub>2</sub>P{OEt}<sub>2</sub>)(S<sub>2</sub>P{OEt}<sub>2</sub>)] where the value of -32.1 ppm has been found for bidentate chelated dppm [24]. The resonances appeared in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **7** and **8** at 55.56 ppm, and 57.37 ppm, respectively, also indicating the coordination of the S<sub>2</sub>P{OR}<sub>2</sub> monoanion to nickel. However, both peaks are significantly shifted downfield with respect to the resonances assigned to bidentate coordination of the ligand ( $\delta \approx 90$  ppm) and thus indicate monodentate ligation with a high possibility. The broadening of the signal observed at 57.37 and 61.97 ppm for **8** can be ascribed both to an existence of paramagnetic species in the CDCl<sub>3</sub> solution [26], *i.e.* the presence of nickel in the high-spin state, and also the possibility that an equi-

librium may exist between diamagnetic, four-coordinated (square-planar) and high-spin, four-coordinated (tetrahedral) complexes. Moreover, an equilibrium between low-spin and high-spin five-coordinated complexes is possible, even if this outcome is less probable in connection with the anticipated monodentate coordination of [S<sub>2</sub>P{OR}<sub>2</sub>]<sup>-</sup>, as was proposed above.

### 3.4. IR and electronic spectra

IR spectra of the complexes **1–8** were measured over the range 150–4000  $\text{cm}^{-1}$ . The bands appearing in the regions of 331–348 and 355–363  $\text{cm}^{-1}$  may be assigned to  $\nu(\text{Ni-S})$  vibrations [3,9]. For comparison, theoretically calculated values for  $\nu(\text{Ni-S})$  in [Ni(S<sub>2</sub>P{OEt}<sub>2</sub>)<sub>2</sub>] are 347.0 and 358.1  $\text{cm}^{-1}$  [27]. The maxima observed between 528 and 536  $\text{cm}^{-1}$  may be assigned to the symmetric P–S vibration while the bands present in the region 654–660  $\text{cm}^{-1}$  are connected with the asymmetric P–S vibration. The strong bands found at 689  $\text{cm}^{-1}$  (for **7**) and 692  $\text{cm}^{-1}$  (for **8**) are shifted to higher frequencies (by  $\approx 30$   $\text{cm}^{-1}$ ) as compared to peaks observed for **1–6**. For this reason, these peaks are attributable to the P=S vibrations. These frequencies are typical for O,O'-dialkylesters of dithiophosphoric acids and their ammonium salts [9]. These findings support, albeit indirectly, the existence of monodentate coordinated [S<sub>2</sub>P{OR}<sub>2</sub>]<sup>-</sup> ligand in the latter two complexes. The presence of a direct bond of NCS<sup>-</sup> to nickel via the nitrogen atom in **7** can be supported by the existence of intensive peaks at 2090, 819 and 483  $\text{cm}^{-1}$ , which may be assigned to  $\nu(\text{C-N})$ ,  $\nu(\text{C-S})$ , and  $\delta(\text{NCS})$  vibrations,



respectively [28]. On the other hand, it is not as easy to prove the coordination of a  $\text{Br}^-$  anion to nickel, as predicted in **8**, even if the stretching vibration belonging to the terminal Ni–Br bond is expected in the region of  $200\text{--}300\text{ cm}^{-1}$  [28]. Moreover, it is known that, the peak position strongly depends on the coordination geometry around nickel, thereby making it difficult to assign specific peaks. However, we assume that the maximum observed at  $295\text{ cm}^{-1}$  in the spectrum of **8** may be correctly assigned to this type of vibration. The bands present in the IR spectra of all the complexes in the regions of  $984\text{--}998\text{ cm}^{-1}$  and  $1042\text{--}1046\text{ cm}^{-1}$  can be attributed to  $\nu[(\text{P})\text{--O}\text{--C}]$  and  $\nu[\text{P}\text{--O}\text{--}(\text{C})]$ , respectively [9]. The ionic nature of the perchlorate anion in complexes **4–6** can be characterized by maxima at approximately  $1104\text{ cm}^{-1}$  [ $\nu_3(\text{ClO}_4)$ ] and  $948\text{ cm}^{-1}$  [ $\nu_4(\text{ClO}_4)$ ] [28].

The assumption of square-planar geometry around the  $\text{Ni}^{\text{II}}$  atoms in **1–7** can also be supported by their electronic spectra. The maxima exhibited at approximately  $19400\text{ cm}^{-1}$  are assignable to the  $^1A_{1g} \rightarrow ^1A_{2g}$  transition, while maxima appearing at approximately  $26000\text{ cm}^{-1}$  can probably be connected with the  $^1A_{1g} \rightarrow ^1B_{1g}$  transition. These observed bands are characteristic for square-planar  $\text{Ni}^{\text{II}}$  complexes with chelated dithiophosphate ligands, as reported in literature data [3,29]. Based on an assumption of tetrahedral geometry, the peaks found in the diffuse-reflectance spectra of the complex **8** at  $14000$  and  $25000\text{ cm}^{-1}$ , may be assigned to the d–d transition  $^3T_1 \rightarrow ^3T_1(\text{P})$  and the spin-forbidden  $^3T_1 \rightarrow ^1T_2$  transition, respectively.

### 3.5. X-ray structures of $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})(\text{dppe})]$ (**1**), $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})(\text{dppb})]\cdot\text{EtOH}$ (**3**) and $[\text{Ni}(\text{S}_2\text{P}\{\text{OEt}\}_2)(\text{dppe})]\text{ClO}_4$ (**5**)

The molecular structures of **1**, **3** and **5** along with the atom numbering scheme are depicted in Figs. 1–3, with selected bond distances and angles given in Tables 4–6. The geometry at the Ni centre in each of the complexes is square-planar with the  $\text{NiP}_2\text{S}_2$  chromophore. The nickel(II) atoms are bound by two phosphorus atoms from one P–P ligand and two sulfur atoms from one O-ethyl phosphorodithioato [in **1** and **3**] or O,O'-diethyl phosphorodithioato ligand [in **5**]. The coordination geometries around nickel are distorted from an ideal arrangement, as can be seen mainly from differences in selected bond angles in the vicinity of the central atom,  $\text{P}(3)\text{--Ni}(1)\text{--S}(1)$ ,  $173.69(2)^\circ$  for **1**,  $175.10(2)^\circ$  for **3**,  $178.14(3)^\circ$  for **5**;  $\text{P}(2)\text{--Ni}(1)\text{--S}(2)$ ,  $173.56(2)^\circ$  for **1**,  $171.21(3)^\circ$  for **3**,  $177.74(3)^\circ$  for **5**;  $\text{S}(2)\text{--Ni}(1)\text{--S}(1)$ ,  $88.70(2)^\circ$  for **1**,  $86.80(2)^\circ$  for **3**,  $89.32(2)^\circ$  for **5**;  $\text{P}(3)\text{--Ni}(1)\text{--P}(2)$ ,  $87.72(2)^\circ$  for **1**,  $95.26(2)^\circ$  for **3**,  $86.22(2)^\circ$  for **5**. It was presumed that the  $\text{P}(3)\text{--Ni}(1)\text{--P}(2)$  angles would be similar in **1** and **5**, however they appear to differ significantly from each other, and increase in **3**.

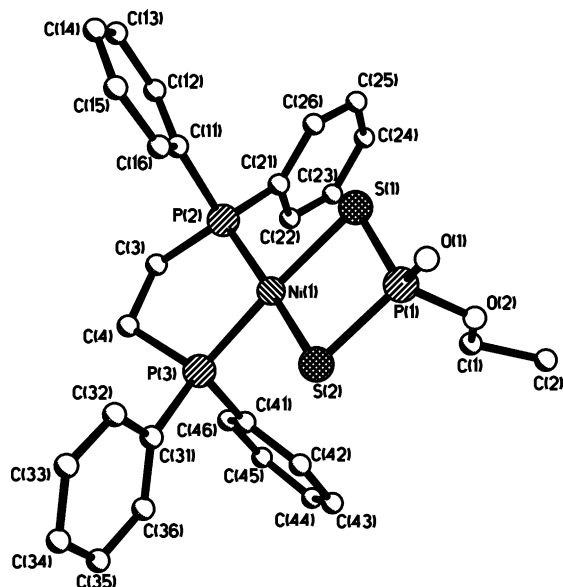


Fig. 1. Molecular structure of  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})(\text{dppe})]$  (**1**). Hydrogen atoms are omitted for the sake of clarity.

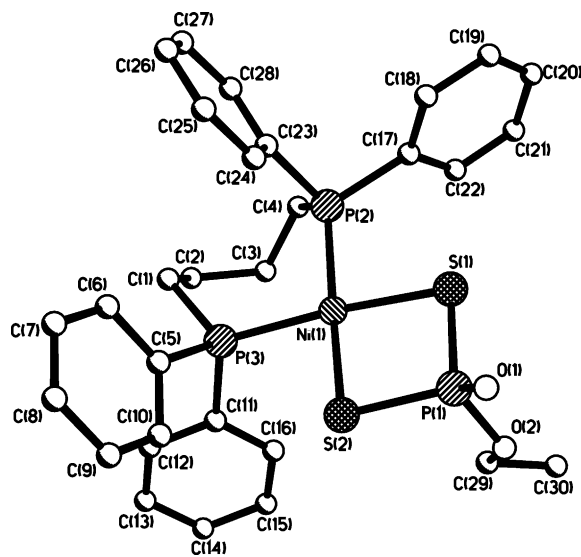


Fig. 2. Molecular structure of  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})(\text{dppb})]\cdot\text{EtOH}$  (**3**). Hydrogen atoms and EtOH are omitted for the sake of clarity.

This enlarged value relates to the longer alkyl string in dppb as compared with dppe. This fact also provides for a substantial decrease in the  $\text{S}(2)\text{--Ni}(1)\text{--S}(1)$  angle and an increase in the  $\text{P}(1)\text{--S}(1)\text{--Ni}(1)$  and  $\text{P}(1)\text{--S}(2)\text{--Ni}(1)$  angles for **3** compared to those values found for **1** and **5** (see Tables 4–6). Owing to the fact that X-ray structures of the nickel complexes with a combination of these specific ligands have not been published, it is impossible, at this point, to perform a comparison of interatomic parameters of the structures presented in this paper with literature data. The molecular structure of similar complex  $[\text{Ni}(\text{dpae})(\text{S}_2\text{P}\{\text{O}\}(\text{OMe}))]$  {dpae = 1-(diphenylarsino)-2-(diphenylphosphino)ethane} was elucidated up

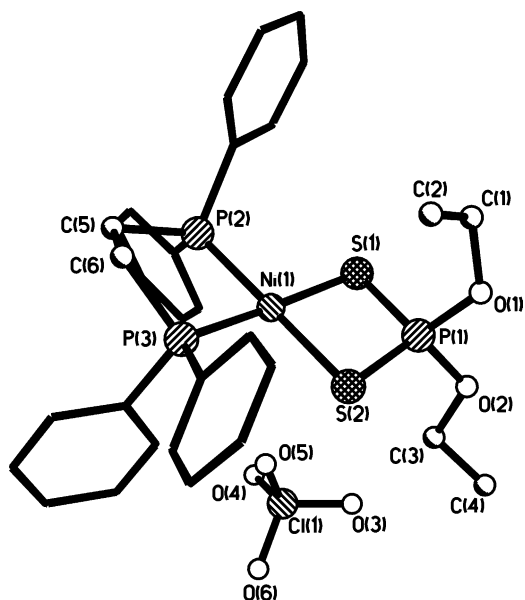


Fig. 3. Molecular structure of  $[\text{Ni}(\text{S}_2\text{P}\{\text{OEt}\}_2)(\text{dppb})]\text{ClO}_4$  (**5**). Hydrogen atoms are omitted for the sake of clarity.

Table 4  
Selected bond lengths [Å] and angles [°] for  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})(\text{dppe})]$  (**1**)

Ni(1)–P(3)	2.1414(6)	P(3)–Ni(1)–P(2)	87.72(2)
Ni(1)–P(2)	2.1608(6)	P(2)–Ni(1)–S(2)	173.56(2)
Ni(1)–S(2)	2.2124(6)	P(3)–Ni(1)–S(1)	173.69(2)
Ni(1)–S(1)	2.2224(6)	S(2)–Ni(1)–S(1)	88.70(2)
S(1)–P(1)	2.0348(8)	O(1)–P(1)–O(2)	105.39(9)
S(2)–P(1)	2.0432(8)	O(1)–P(1)–S(1)	117.62(8)
P(1)–O(1)	1.4757(16)	O(2)–P(1)–S(1)	109.02(7)
P(1)–O(2)	1.6053(15)	O(1)–P(1)–S(2)	116.46(7)
P(2)–C(11)	1.816(2)	O(2)–P(1)–S(2)	109.12(6)
P(2)–C(21)	1.815(2)	S(1)–P(1)–S(2)	98.97(3)
P(2)–C(3)	1.840(2)	C(4)–P(3)–Ni(1)	108.36(7)
P(3)–C(41)	1.813(2)	C(1)–O(2)–P(1)	121.82(14)
P(3)–C(31)	1.816(2)	O(2)–C(1)–C(2)	107.4(2)
P(3)–C(4)	1.838(2)	C(4)–C(3)–P(2)	109.01(15)
O(2)–C(1)	1.451(3)	C(3)–C(4)–P(3)	110.25(15)
C(1)–C(2)	1.505(3)	P(1)–S(1)–Ni(1)	85.72(3)
C(3)–C(4)	1.522(3)	P(1)–S(2)–Ni(1)	85.79(3)

to now [15]. Thus, the interatomic parameter values around the nickel core in **1** are comparable to those determined for  $[\text{Ni}(\text{dpae})(\text{S}_2\text{P}\{\text{O}\}\text{OMe})]$  (Ni–S, 2.209(3) and 2.210(3) Å; Ni–P, 2.185(3) Å and S(1)–Ni–S(2), 88.4(1)°). The  $[\text{Ni}(\text{dppe})(\text{pipdte})](\text{ClO}_4)$  [25] and  $[\text{Ni}(\text{dppb})(\text{plddtc})]\text{I}\cdot\text{H}_2\text{O}$  {plddtc = pyrrolidinedithiocarbamate anion} [30] complexes bearing the same chromophore and coordination geometry have also been structurally characterized.

#### 4. Conclusions

Although numerous five and six-coordinated mononuclear nickel(II) dithiophosphate complexes with ni-

Table 5  
Selected bond lengths [Å] and angles [°] for  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})(\text{dppb})]\cdot\text{EtOH}$  (**3**)

Ni(1)–P(2)	2.1969(6)	P(2)–Ni(1)–P(3)	95.26(2)
Ni(1)–P(3)	2.2068(6)	P(3)–Ni(1)–S(1)	175.10(2)
Ni(1)–S(1)	2.2081(6)	P(2)–Ni(1)–S(2)	171.21(3)
Ni(1)–S(2)	2.2270(6)	S(1)–Ni(1)–S(2)	86.80(2)
S(1)–P(1)	2.0402(8)	P(1)–S(1)–Ni(1)	88.42(3)
S(2)–P(1)	2.0364(8)	P(1)–S(2)–Ni(1)	88.00(3)
P(1)–O(1)	1.4802(16)	O(1)–P(1)–O(2)	106.30(9)
P(1)–O(2)	1.5954(16)	O(1)–P(1)–S(2)	116.64(8)
P(2)–C(23)	1.824(2)	O(2)–P(1)–S(2)	109.08(7)
P(2)–C(17)	1.831(2)	O(1)–P(1)–S(1)	117.71(8)
P(2)–C(4)	1.845(2)	O(2)–P(1)–S(1)	110.02(7)
P(3)–C(11)	1.827(2)	S(2)–P(1)–S(1)	96.75(3)
P(3)–C(5)	1.827(2)	C(2)–C(1)–P(3)	114.01(17)
P(3)–C(1)	1.841(2)	C(3)–C(2)–C(1)	115.5(2)
O(2)–C(29)	1.455(3)	C(2)–C(3)–C(4)	114.7(2)
O(3)–C(31)	0.832(16)	C(3)–C(4)–P(2)	116.21(17)
O(4)–C(31)	1.032(11)	C(6)–C(5)–P(3)	120.58(19)
C(1)–C(2)	1.528(3)	C(18)–C(17)–P(2)	120.74(18)
C(2)–C(3)	1.516(3)	C(22)–C(17)–P(2)	120.91(19)
C(3)–C(4)	1.531(3)	C(24)–C(23)–P(2)	117.93(17)
		C(28)–C(23)–P(2)	123.79(18)

Table 6  
Selected bond lengths [Å] and angles [°] for  $[\text{Ni}(\text{S}_2\text{P}\{\text{OEt}\}_2)(\text{dppe})]\text{ClO}_4$  (**5**)

Ni(1)–P(3)	2.1550(6)	P(3)–Ni(1)–P(2)	86.22(2)
Ni(1)–P(2)	2.1680(6)	P(2)–Ni(1)–S(2)	177.74(3)
Ni(1)–S(2)	2.2272(6)	P(3)–Ni(1)–S(1)	178.14(3)
Ni(1)–S(1)	2.2410(6)	S(2)–Ni(1)–S(1)	89.32(2)
Ni(1)–P(1)	2.8085(6)	P(3)–Ni(1)–P(1)	136.38(2)
S(1)–P(1)	1.9964(8)	P(2)–Ni(1)–P(1)	136.58(2)
S(2)–P(1)	1.9954(8)	S(2)–Ni(1)–P(1)	44.87(2)
P(1)–O(1)	1.5670(17)	S(1)–Ni(1)–P(1)	44.85(2)
P(1)–O(2)	1.5724(17)	P(1)–S(1)–Ni(1)	82.81(3)
P(2)–C(21)	1.813(2)	P(1)–S(2)–Ni(1)	83.19(3)
P(2)–C(11)	1.817(2)	O(1)–P(1)–O(2)	97.75(9)
P(2)–C(5)	1.845(2)	O(1)–P(1)–S(2)	113.69(7)
P(3)–C(31)	1.808(2)	O(2)–P(1)–S(2)	114.27(8)
P(3)–C(41)	1.809(2)	O(1)–P(1)–S(1)	112.57(7)
P(3)–C(6)	1.833(2)	O(2)–P(1)–S(1)	115.26(7)
O(1)–C(1)	1.488(3)	S(2)–P(1)–S(1)	103.77(3)
O(2)–C(3)	1.477(3)	O(1)–P(1)–Ni(1)	123.36(7)
C(1)–C(2)	1.437(5)	O(2)–P(1)–Ni(1)	138.89(7)
C(3)–C(4)	1.433(5)	S(2)–P(1)–Ni(1)	51.94(2)
C(5)–C(6)	1.530(3)	S(1)–P(1)–Ni(1)	52.34(2)
		C(1)–O(1)–P(1)	124.09(16)
		C(3)–O(2)–P(1)	119.52(16)
		C(2)–C(1)–O(1)	114.3(3)
		C(4)–C(3)–O(2)	109.4(3)
		C(6)–C(5)–P(2)	109.78(16)
		C(5)–C(6)–P(3)	106.57(16)

trogen donor ligands are known in the literature, examples of such structural varieties with phosphorus donor ligands are quite uncommon. On the basis of the above studies, including the X-ray structures of  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})(\text{dppe})]$ ,  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}\}\text{OEt})(\text{dppb})]\cdot\text{EtOH}$  and  $[\text{Ni}(\text{S}_2\text{P}\{\text{OEt}\}_2)(\text{dppe})]\text{ClO}_4$ , we conclude that tetracoor-

minated complexes with square-planar geometry around nickel have been prepared. For  $[\text{Ni}(\text{S}_2\text{P}\{\text{OEt}\}_2)(\text{dppe})\text{Br}] \cdot \text{H}_2\text{O}$ , the suggested tetrahedral geometry probably relates to a monodentate coordination of a  $\text{S}_2\text{P}\{\text{OEt}\}_2$  monoanion. This mode of the  $\text{S}_2\text{P}\{\text{OEt}\}_2$  ligand coordination has also been proposed in  $[\text{Ni}(\text{S}_2\text{P}\{\text{O}-i\text{-Pr}\}_2)(\text{dppe})(\text{NCS})]$ .

## 5. Supplementary material

Crystallographic data of the structures presented in this paper have been deposited with the Cambridge Crystallographic Data Centre (The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk; www: <http://www.ccdc.cam.ac.uk>; fax: +44-1223-336033) and are available free of charge on request, quoting the deposition numbers 197179 for **1**, 197180 for **3** and 197181 for **5**.

## Acknowledgements

The authors would like to thank Dr. Zdeněk Šindelář for magnetochemical measurements and Mr. Michal Maloň for providing  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra. The crystallographic part of this work was supported by the GACR (a Grant No. 203/02/0436).

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