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Polyhedron 26 (2007) 2672-2678

Synthesis, characterization and spectral studies of nitrogen base adducts of bis(O,O'-ditolyldithiophosphato)nickel(II). Crystal structures of Ni[S₂P(OC₆H₄Me-p)₂]₂ · C₁₀H₈N₂ and Ni[S₂P(OC₆H₄Me-o)₂]₂ · C₁₄H₁₂N₂ · C₆H₆

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> Received 18 December 2006; accepted 10 January 2007 Available online 14 January 2007

Abstract

Reactions of Ni[S₂P(OR)₂]₂(R = o-, m- and p-C₆H₄Me) with nitrogen donor ligands, viz. pyridine (C₅H₅N or py), 2,2'-bipyridyl (C₁₀H₈N₂ or bipy) and 2,9-dimethyl-1,10-phenanthroline (C₁₄H₁₂N₂ or dmphen) were carried out in benzene to yield green paramagnetic solids. These adducts were characterized by UV-visible and IR spectroscopy, magnetic measurements and, in two cases, by X-ray crystallography, to indicate how the number of donor atoms and steric factors affect the Ni–S bonding. The molecular structures of 2,2'-bipyridylbis {O,O'-di(p-tolyl)dithiophosphate}nickel(II), Ni[S₂P(OC₆H₄Me-p)₂]₂ · C₁₀H₈N₂ and 2,9-dimethyl-1,10-phenanthroline-bis{O,O'-di(p-tolyl)dithiophosphate}nickel(II), Ni[S₂P(OC₆H₄Me-p)₂]₂ · C₁₄H₁₂N₂ · C₆H₆ are described. The geometry around nickel in the bipyridyl adduct is distorted octahedral with NiS₄N₂ coordination, whereas in the 2,9-dimethyl-1,10-phenanthroline adduct it is trigonal bipyramidal with NiS₃N₂ coordination in which one dithiophosphate moiety is bidentate and the other is monodentate. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Synthesis; Nickel adducts; Structure; 2,2'-Bipyridyl; 2,9-Dimethyl-1,10-phenanthroline

1. Introduction

The coordination chemistry of nickel with dialkyl(acyclic) [1–5] and alkylene(cyclic) [6–12] dithiophosphate ligands has been explored extensively in the past three decades yielding several four coordinate square planar complexes. These square planar complexes can be stabilized by the formation of adducts with neutral donor ligands to yield five and six coordinate adducts. Adducts of nickel (II) dithiophosphate with nitrogen donor ligands have been used as antioxidants and antiwear additives in the rubber

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industry [13] and for their insecticidal activity [14]. Syntheses, along with extensive spectroscopic studies, have been reported for nickel(II) dithiophosphate adducts with monodentate nitrogen base ligands such as pyridine (py), 4-picoline, and primary amines [9,15–17] as well as with bidentate ligands such as bipyridyl ($C_{10}H_8N_2$ or bipy), phe-2.9-dimethyl-1,10-phenanthroline nanthroline (phen). (C₁₄H₁₂N₂ or dmphen) and aromatic primary diamines [8,16–20]. X-ray structures have been reported for Ni[S₂P- $(OEt)_2_2(py)_2$ [21], Ni[S₂P(OPr')_2_2(py)_2 [22], Ni[S₂P- $(OPr^{i})_{2}$ [2-aminopyridine-N)₂ [23], Ni[S₂P(OMe)₂]₂(phen) [24], Ni[S₂P(OBuⁿ)₂]₂(bipy) [25], Ni[S₂P(OMe)₂]₂(dmphen) [24], Ni[S₂P(OCMe₂CMe₂O)₂]₂(dmphen) [26] and Ni[S₂P- $(OC_6H_4Me_{-p})_2]_2(phen)$ [27].

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The continuation of our interest in various dithiophosphate ligands led us to work on the reactions of aryl dithiophosphate nickel complexes with nitrogen donor moieties to examine how the aromatic moiety influences coordination with the metal. Thus, we report the syntheses of nickel (II) adducts of the general type Ni[S₂P(OR)₂]₂ · *n*L (where R = o-, *m*-, *p*-C₆H₄Me; n = 2, $L = C_5H_5N$; n = 1, $L = C_{10}H_8N_2$, $C_{14}H_{12}N_2$) and their characterization by various spectroscopic techniques. We also report the molecular structures of Ni[S₂P(OC₆H₄Me-*p*)₂]₂ · C₁₀H₈N₂ and Ni[S₂P-(OC₆H₄Me-*o*)₂]₂ · C₁₄H₁₂N₂ · C₆H₆.

2. Results and discussion

Reactions of bis (O,O'-ditolyldithiophosphato)nickel(II) complexes were carried out with pyridine or 2,2'-bipyridyl or 2,9-dimethyl-1,10-phenanthroline in benzene

$$\operatorname{Ni}[S_2 P(OR)_2]_2 + nL \to \operatorname{Ni}[S_2 P(OR)_2]_2 \cdot nL$$
(1)

 $(R = o-, m-, p-C_6H_4Me; n = 2, L = C_5H_5N; n = 1, L = C_{10}H_8N_2, C_{14}H_{12}N_2)$

The purple colour changed on addition of nitrogen base to give a consistent green colour on addition of a slight excess of base. In each case a green powder (yield, 67– 78%), soluble in organic solvents, was obtained.

2.1. IR spectra

The IR spectra of the nitrogen base adducts of bis(O,O'ditolyl dithiophosphato)nickel(II) were measured over the range of 4000–200 cm⁻¹. The assignments of the relevant IR bands (Table 1) were made by comparisons with the spectra of the corresponding nickel(II) O,O'-ditolyldithiophosphate complexes [28]. The two strong intensity bands present in the 1168–1123 and 841–790 cm⁻¹ regions are assigned to v[(P)-O-C] and v[P-O-(C)] stretching vibrations, respectively. Bands due to $v(P-S)_{asym}$ and $v(P-S)_{sym}$ observed at 693–656 and 568–516 cm⁻¹ in adducts 1–9, indicate a slight change in the bonding patterns of the dithiophosphate moieties upon adduct formation. However, in case of dmphen adducts, 7–9 additional bands corresponding to $v(P-S)_{asym}$ and $v(P-S)_{sym}$ are also observed suggesting the S-mondentate and S,S-chelating nature of the ligands. The presence of medium to weak bands in the regions 380-362 and 344-324 cm⁻¹ have been assigned to v(Ni-S) vibrations consistent with the metal sulfur bonding. One or two peaks due to v(C-N) vibrations appears in the region 1604-1579 cm⁻¹ suggests the formation of adducts.

2.2. UV-visible spectra

The spectra of the adducts of bis(O,O'-ditolyl dithiophosphato)nickel(II) recorded in CH₂Cl₂ (Table 2) show three absorption bands corresponding to ${}^{3}A_{2}g \rightarrow {}^{3}T_{2}g$, ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(F)$, ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(P)$ transitions expected for octahedral nickel species [16,18]. The first band corresponding to ${}^{3}A_{2}g \rightarrow {}^{3}T_{2}g$ transition is obtained in the range of 1102–1130 nm. The second absorption ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(F)$ is observed in the range 727–735, 654–658 for pyridine and bipyridyl adducts, respectively but split in two absorptions in the range 676–686 and 866–886 nm for 2,9-dimethyl-1,10-phenanthroline adducts. This split is probably due to spin-orbit coupling of ${}^{1}E(D)$ with ${}^{3}T_{1}g$. The third band, ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g$ is seen in the range of 447–451, 416–422 and 423–441 nm for pyridine, bipyridyl and 2,9-dimethyl-1,10-phenanthroline adducts, respectively.

2.3. Magnetic moments measurements

The magnetic measurements (Table 2) for nitrogen base adducts of bis(O,O'-ditolyldithiophosphato)nickel(II)obtained in the range of 3.20–3.26 BM at 298 K indicate the presence of two unpaired electrons. Similar values are found in the literature for a number of other bis(O,O'-ditolyldithiophosphato)nickel(II) adducts [16].

2.4. Molecular structures of $Ni[S_2P(OC_6H_4Me-p)_2]_2 \cdot C_{10}H_8N_2$ (6) and $Ni[S_2P(OC_6H_4Me-o)_2]_2 \cdot C_{14}H_{12}N_2 \cdot C_6H_6$ (7)

Ni[S₂P(OC₆H₄Me-p)₂]₂ · C₁₀H₈N₂ (**6**) and Ni[S₂P-(OC₆H₄Me-o)₂]₂ · C₁₄H₁₂N₂ · C₆H₆ (**7**), crystallize as triclinic and monoclinic in space groups $P\bar{1}$ and $P2_1/c$, respectively. The ORTEP diagrams in Figs. 1 and 2 illustrate that in **6** the nickel atom lies at the centre of a

Table 1

IR spectral data (cm^{-1}) for the nitrogen base adducts of bis(O, O'-ditolyldithiophosphate)nickel(II) complexes^a

No.	Compound	v(C–N)	v[(P)–O–C]	v[P–O–(C)]	v(P-S)asym.	$v(P-S)_{sym}$	v(Ni–S)
1	$Ni[S_2P(OC_6H_4Me-o)_2]_2(C_5H_5N)_2$	1585 m	1142 s	820 s	682 s	555 m	370 w, 324 w
2	$Ni[S_2P(OC_6H_4Me-m)_2]_2(C_5H_5N)_2$	1584 s	1123 s	824 s	687 s	568 m	365 w, 325 w
3	$Ni[S_2P(OC_6H_4Me-p)_2]_2(C_5H_5N)_2$	1598 m	1162 m	822 s	693 m	535 s	370 w, 333 w
4	$Ni[S_2P(OC_6H_4Me-o)_2]_2 \cdot N_2C_{10}H_8$	1581, 1603 m	1130 s	831 s	681 s	565 m	367 w, 344w
5	$Ni[S_2P(OC_6H_4Me-m)_2]_2 \cdot N_2C_{10}H_8$	1590 m	1130 s	831 s	685 s	564 m	362 w, 327w
6	$Ni[S_2P(OC_6H_4Me-p)_2]_2 \cdot N_2C_{10}H_8$	1595, 1604 m	1153 m	812 m	680 s	556 m	377 w, 328 w
7	$Ni[S_2P(OC_6H_4Me-o)_2]_2 \cdot N_2C_{14}H_{12}$	1579 m	1167 s	790 m 674 m,	657 m	549 sh	380 m, 330 m
8	$Ni[S_2P(OC_6H_4Me-m)_2]_2 \cdot N_2C_{14}H_{12}$	1590 m	1139 m	841 m 680 m,	665 m	560 sh	377 w, 328 w
9	$Ni[S_2P(OC_6H_4Me-p)_2]_2 \cdot N_2C_{14}H_{12}$	1580, 1592 m	1168 s	790 s	672 s, 656,m	550 m, 516 m	378 w, 325 w

^a Key: s = strong, m = medium, w = weak, sh = shoulder.

Table 2

Electronic spectra and magnetic moments for the nitrogen base adducts of bis(O,O'-ditolyldithiophosphate)nickel(II) complexes

S. no.	Compound	Λ_{max} (nm)	$\mu_{\rm eff} ({ m BM})$
1	$Ni[S_2P(OC_6H_4Me-o)_2]_2(C_5H_5N)_2$	1120, 735, 451	3.20
2	$Ni[S_2P(OC_6H_4Me-m)_2]_2(C_5H_5N)_2$	1110, 727, 447	3.19
3	$Ni[S_2P(OC_6H_4Me-p)_2]_2(C_5H_5N)_2$	1130, 734, 449	3.22
4	$Ni[S_2P(OC_6H_4CH_3-o)_2]_2 \cdot N_2C_{10}H_8$	1130, 658, 418	3.23
5	$Ni[S_2P(OC_6H_4CH_3-m)_2]_2 \cdot N_2C_{10}H_8$	1114, 656, 416	3.21
6	$Ni[S_2P(OC_6H_4CH_3-p)_2]_2 \cdot N_2C_{10}H_8$	1102, 654, 422	3.23
7	$Ni[S_2P(OC_6H_4CH_3-o)_2]_2 \cdot N_2C_{14}H_{12}$	1105, 676, 430	3.25
8	$Ni[S_2P(OC_6H_4CH_3-m)_2]_2 \cdot N_2C_{14}H_{12}$	1125, 676, 441	3.23
9	$Ni[S_2P(OC_6H_4CH_3-p)_2]_2 \cdot N_2C_{14}H_{12}$	1110, 686, 423	3.24

distorted octahedral, NiN₂S₄, chromophore whereas in 7 the geometry around nickel is that of a distorted trigonal bipyramidal, NiN₂S₃ chromophore. Solvent benzene molecules are also incorporated into the crystal of the latter. In 6 the square planar structure of Ni[$S_2P(OC_6H_4Me$ p_{2} [29] has readily accommodated the introduction of bipy while maintaining the integrity of the two bidentate S₂P(OC₆H₄Me-*p*)₂ ligands, as was also found for Ni[S₂- $P(OC_6H_4Me-p)_2$ (phen) [27]. By contrast, in 7 the analogous distorted square planar structure of Ni[S2- $P(OC_6H_4Me-o)_2$ [28] with two bidentate ligands is not maintained in the presence of dmphen because the cleavage of one Ni-S bond results in the formation of a monodentate ligand. The presence of methyl groups in 7 on the nitrogen base, dmph increases the crowding near Ni atom resulting the cleavage of one Ni-S bond. Hence one of the ligand is rendered as monodentate and other as bidentate. The cis orientation of the nitrogen donor atoms is also responsible for this cleavage.

In Ni[S₂P(OC₆H₄Me-p)₂]₂(C₁₀H₈ N₂) (**6**), all four Ni–S bond lengths are fairly similar (2.4757(7) to 2.5096(6) Å)

in the two bidentate dithiophosphate ligands and in the range of other analogous six-coordinated compounds, $Ni[S_2P(OBu^n)_2]_2(bipv)$ (2.463(2)-2.524(2) Å) [25]. $Ni[S_2 P(OMe)_2$ (phen) (2.47(1)-2.52(1) Å) [24] and Ni[S₂P- $(OC_6H_4Me_{-p})_2$ (phen) (2.486(1)-2.532(1) Å) [27]. The distances are significantly larger and cover a larger range than in the four-coordinate precursors Ni[S₂P(OC₆H₄Me p_{2}_{2} (average 2.332(2) Å) [29] and Ni[S₂P(OC₆H₄Me- $o_{2}_{2}_{2}$ (average 2.233(8) Å) [28]. By contrast, in Ni[S₂P(OC₆H₄- $Me-o_{2} \ge (C_{14}H_{12}N_{2}) \cdot C_{6}H_{6}$ (7), the bidentate dithiophosphate ligand, with Ni-S bond lengths of 2.352(1) and 2.539(1) Å, might more accurately be defined as anisobidentate, while the second dithiophosphate ligand is clearly monodentate with Ni(1)–S(3) at 2.386(1) Å and Ni(1)–S(4) at 5.462(2) Å. The closest approach of this pendant S atom to the Ni atom of the nearest adjacent molecule is 7.208(2) Å. Similar behavior is seen in the analogous fivecoordinate complexes, $Ni[S_2P(OMe)_2]_2(dmphen)$ [24] and Ni[S₂P(OCMe₂CMe₂O)₂]₂(dmphen) [26], with the monodentate Ni-S bonds 2.42(1) and 2.398(3) Å, respectively, and the (aniso)bidentate ligands having Ni-S distances ranging from 2.30(1) to 2.58(1) Å. The Ni–N bond lengths are similar in 6 (2.060(1) and 2.079(1) Å) and 7 (2.010(1)) and 2.009(1) Å) which is in good agreement with the distances found in the six-coordinate analogues, Ni[S2P- $(OBu^{n})_{2}_{2}(bipy)$ (2.088(4) and 2.089(4) Å) [25], Ni[S₂P- $(OMe)_2$ (phen) (2.08(1) and 2.09(1) Å) [24] and Ni[S₂₋ $P(OC_6H_4Me_{-p})_2]_2$ (phen) (2.082(3) and 2.086(3) Å) [27] as well as in the five-coordinate analogues Ni[S₂P- $(OMe)_2_2(dmphen)$ (1.97(1) and 2.03(1) Å) [24] and Ni[S₂P- $(OCMe_2CMe_2O)_2]_2(dmphen)$ (2.005(8) and 2.015(7) Å) [26]. Although the differences are small, the trend of slightly shorter Ni-N bonds in the five coordinate complexes is clear and suggestive of slightly stronger bonding



Fig. 1. ORTEP plot of the molecule $Ni[S_2P(OC_6H_4Me-p)_2]_2 \cdot C_{10}H_8N_2$. The non-hydrogen atoms are drawn with 50% probability ellipsoids.



Fig. 2. ORTEP plot of Ni[S₂P(OC₆H₄Me-o)₂]₂ · C₁₄H₁₂N₂ · C₆H₆. The non-hydrogen atoms are drawn with 25% probability ellipsoids and the benzene molecule is omitted for clarity.

when accommodation has been made to incorporate the bulkier nitrogen ligand by the cleavage of an Ni-S bond and reorientation of the resulting monodentate sulfur ligand. The average lengths of the four P-S bonds in 6 are the same as in Ni[S₂P(OC₆H₄Me-p)₂]₂ (average 1.973(6) Å) which suggests that the competitive chelation of sulfur and nitrogen donor atoms has no significant influence on the partial double bond character of these P-S bonds. In 7, the P(2)-S(4) bond of the pendant, non-interacting sulfur atom is by far the shortest (1.941(2) Å), with the P(1)-S(2) bond associated with the much longer Ni(1)-S(2) bond in the anisobidentate ligand being somewhat longer (1.969(2) Å). The P(1)–S(1) associated with the shorter Ni(1)–S(1) anisobidentate bond and the P(1)–S(3) associated with the monodentate Ni(1)-S(3) bond are longer and essentially the same, 1.997(2) and 1.995(2) Å, respectively.

In Ni[S₂P(OC₆H₄Me-*p*)₂]₂(C₁₀H₈ N₂) (**6**), the S–Ni–S ligand bite angles of 81.33(2) and 81.99(2)° are similar to the values observed in Ni[S₂P(OBu^{*n*})₂]₂(bipy) (81.40(7) and 81.63(7)°) [25], Ni[S₂P(OMe)₂]₂(phen) (81.3(2)° and 81.6(2)°) [24] and Ni[S₂P(OC₆H₄Me-*p*)₂]₂(phen) (81.13 and 81.57(2)°) [27]. The bite angle of the chelating ligand in Ni[S₂P(OC₆H₄Me-*o*)₂]₂ · C₁₄H₁₂N₂ · C₆H₆ (**7**) is similar (82.05(4)°) and comparable to that in Ni[S₂P(OMe)₂]₂ · dmphen (81.7(1)° [24] and Ni[S₂POCMe₂CMe₂O)₂]₂ · dmphen (82.1(1)°) [26]. The N–Ni–N bite angles of 79.10(5)° in **6** and 82.6(2)° in **7**, are typical of the values found in the corresponding six-coordinate, Ni[S₂P(OBu^{*n*})₂]₂ · bipy,

 $Ni[S_2P(OMe)_2]_2$ · phen and $Ni[S_2P(OC_6H_4Me-p)_2]_2$ · phen (average 79.4(3)°) and five coordinate analogues Ni[S₂P- $(OCMe_2CMe_2O)_2]_2 \cdot dmphen and Ni[S_2P(OMe)_2]_2 \cdot dm$ phen (average $82.5(0.3)^\circ$), respectively. In 6, the least deviation from 180° involves the two shorter (stronger) Ni–S bonds in the bidentate ligands (S(1)–N(1)–S(4)) $(173.09(2)^{\circ})$, while those involving the donor and the longer Ni-S bonds are slightly more deviated with N-Ni-S angles of $171.63(4)^{\circ}$ and $168.03(4)^{\circ}$. The three cis S–Ni–S angles, other than the ligand bite angles, cover the range 91.33-93.53°, whereas the six involving S-Ni-N angles range from $88.41(4)^{\circ}$ to $97.18(4)^{\circ}$. In 7, the axial positions of the distorted trigonal bipyramid are occupied by the Ni-S bond of the monodentate ligand and the longer Ni-S bond of the (aniso)bidentate ligand (S(2)-Ni(1)-S(3)) $167.05(5)^{\circ}$). The sum of the three angles in the trigonal (S(1)-Ni(1)-N(1))134.3(1)°, plane S(1)-Ni(1)-N(2) $142.1(1)^{\circ}$ and N(1)-Ni(1)-N(2) 82.6(2)^{\circ} is 359.1°. The dmphen group is also essentially in the equatorial plane. Similar corresponding angles have been reported for Ni[S2- $POCMe_2CMe_2O_2_2 \cdot dmphen$ (axial S-Ni-S 169.1(1)°; equatorial S-Ni-N 131.1(3)°, S-Ni-N 144.3(2)° and N1-Ni–N 82.5(3)°) [26] and Ni[S₂P(OMe)₂]₂ · dmphen (axial S-Ni-S 165.8(1)°; equatorial S-Ni-N 130.2(3)°, S-Ni-N 145.7(2)° and N1-Ni-N 82.4(43)°) [24].

In **6** the S–P–S bond angles for the bidentate ligands are $110.34(2)^{\circ}$ and $112.53(3)^{\circ}$ as was reported for the six-coordinate analogues Ni[S₂P(OC₆H₄Me-*p*)₂]₂ · phen $(110.37(6)-112.81(5)^{\circ})$ [27] and Ni[S₂P(OMe)₂]₂ · phen

 $(110.8(2)-111.6(2)^{\circ})$ [24]. In 7, the two angles differ considerably with the S–P–S bond angle of $116.1(1)^{\circ}$ for the monodentate ligand being considerably larger than that of the (aniso)bidentate ligand ($108.27(8)^{\circ}$). These values are similar to those found in the analogous five-coordinated complexes, Ni[S₂P(OMe)₂]₂ · dmphen ($116.9(2)^{\circ}$ and $111.1(2)^{\circ}$) [24] and Ni[S₂P(OCMe₂CMe₂O)₂]₂ · dmphen ($117.2(2)^{\circ}$ and $108.0(2)^{\circ}$) [26].

3. Experimental

Solvents (benzene, dichloromethane, *n*-hexane, diethyl ether) were dried by standard methods before use. All reactions were carried out in pre-dried glassware under anhydrous conditions. Literature methods were used for the preparation of bis(O,O'-ditolyldithiophosphato)nickel(II) [28] and ammonium salts of O,O-ditolyldithiophosphoric acids [30,31].

3.1. Preparations

3.1.1. $Ni[S_2P(OC_6H_4Me-o)_2]_2 \cdot 2C_5H_5N(1)$

Ni[S₂P(OC₆H₄Me-o)₂]₂ (0.489 g, 0.723 mmol) was dissolved in dry benzene (20 ml). Pyridine was added until the purple colour of the solution changed to green. The solution was concentrated under vacuo. Diethylether was added to the concentrated solution to obtain a green precipitate. The adduct was recrystallized using a dichloromethane/ether mixture (1:2 v/v). Yield: 0.328 g, 67%. *Anal.* Calc. for C₃₈H₃₈O₄N₂S₄P₂Ni: Ni, 7.02; S, 15.35. Found: Ni, 6.83; S, 15.17%.

3.1.2. $Ni[S_2P(OC_6H_4Me-m)_2]_2 \cdot 2C_5H_5N(2)$

Method as above gave a green powdery solid. Yield: 0.401 g, 73%. *Anal.* Calc. for $C_{38}H_{38}O_4N_2S_4P_2Ni$: Ni, 7.02; S, 15.35. Found: Ni, 6.94; S, 15.48%.

3.1.3. Ni[S₂P(OC₆H₄Me-p)₂]₂ · 2C₅H₅N (**3**) Yield: 0.205 g, 69%. *Anal.* Calc. for C₃₈H₃₈O₄N₂S₄P₂Ni: Ni, 7.02; S, 15.35. Found: Ni, 7.10; S, 15.51%.

3.1.4. $Ni[S_2P(OC_6H_4Me-o)_2]_2 \cdot C_{10}H_8N_2$ (4) Yield: 0.263 g, 78.2%. Anal. Calc. for $C_{38}H_{36}O_4N_2$ - S_4P_2Ni : Ni, 7.04; S, 15.39. Found: Ni, 7.25; S, 15.52%.

3.1.5. $Ni[S_2P(OC_6H_4Me-m)_2]_2 \cdot C_{10}H_8N_2$ (5) Yield: 0.349 g, 74%. *Anal.* Calc. for $C_{38}H_{36}O_4N_2S_4P_2Ni$: Ni, 7.04; S, 15.39. Found: Ni, 7.25; S, 15.72%.

3.1.6. $Ni[S_2P(OC_6H_4Me-p)_2]_2 \cdot C_{10}H_8N_2$ (6) Yield: 0.357 g, 77.5%. Anal. Calc. for $C_{38}H_{36}O_4N_2$ - S_4P_2Ni : Ni, 7.04; S, 15.39. Found: Ni, 7.11; S, 15.48%.

3.1.7. $Ni[S_2P(OC_6H_4Me-o)_2]2 \cdot C_{14}H_{12}N_2$ (7) Yield: 0.288 g, 69.7%. *Anal.* Calc. for $C_{42}H_{40}O_4N_2$ - S_4P_2Ni : Ni, 6.84; S, 14.96. Found: Ni, 6.75; S, 14.72%. 3.1.8. $Ni[S_2P(OC_6H_4Me-m)_2]_2 \cdot C_{14}H_{12}N_2$ (8)

Yield: 0.321 g, 71.9%. Anal. Calc. for $C_{42}H_{40}O_4N_2$ -S₄P₂Ni: Ni, 6.84; S, 14.96. Found: Ni, 6.81; S, 14.90%.

3.1.9. $Ni[S_2P(OC_6H_4Me-p)_2]_2 \cdot C_{14}H_{12}N_2$ (9) Yield: 0.426 g, 73.4%. *Anal.* Calc. for $C_{42}H_{40}O_4N_2$ - S_4P_2Ni : Ni, 6.84; S, 14.96. Found: Ni, 6.79; S, 14.87%.

3.2. Physical measurements

Sulfur was estimated gravimetrically as barium sulfate (Messengers method) and nickel as dimethylglyoximate. IR spectra were recorded in the range 4000–200 cm⁻¹ on a Perkin–Elmer 983G spectrophotometer (Nujol mull). Electronic spectra in the range 200–1200 nm were recorded on a Perkin Elmer UV/VIS/NIR spectrometer-Lambda 19 in CH₂Cl₂. The magnetic measurements at 298 K were determined using the Evans NMR method [32].

T_{a1}	hla	3	
1 a	Die	3	

Crystal data and structure refinements for $Ni[S_2P(OC_6H_4Me-p)_2]_2 \cdot C_{10}H_8N_2$ and $Ni[S_2P(OC_6H_4Me-a)_2]_2 \cdot C_{14}H_{12}N_2 \cdot C_6H_6$

Empirical formula	C ₃₈ H ₃₆ O ₄ N ₂ P ₂ S ₄ Ni	$C_{48}H_{46}O_4N_2P_2S_4N_1$
Formula weight	833.58	963.76
Temperature (K)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\overline{1}$	$P2_1/c$
<i>a</i> (Å)	10.8219(7)	13.950(1)
b (Å)	12.035(3)	22.697(2)
c (Å)	16.737(3)	14.4965(7)
α (°)	70.73(1)	
β (°)	75.004(9)	90.050(6)
γ (°)	70.752(8)	
Volume (Å ³)	1915.1(5)	4589.8(5)
Z	2	4
Density (calculated) (g/cm ³)	1.446	1.395
Absorption coefficient (mm ⁻¹)	0.851	0.721
<i>F</i> (000)	864	2008
Crystal size (mm ³)	$0.20\times0.10\times0.10$	$0.20\times0.14\times0.07$
θ Range for data collection (°)	3.30-27.55	3.06-25.08
Index ranges	$-14 \leq h \leq 13$,	$-16 \leq h \leq 16$,
	$-15 \leq k \leq 15$,	$-26 \leq k \leq 27$,
	$-21 \leq l \leq 21$	$-17 \leq l \leq 15$
Reflections collected	40 0 6 4	41 699
Independent reflections $[R_{int}]$	8756 [0.0289]	8062 [0.1040]
Max. and min. transmission	0.9197 and 0.8483	0.9513 and 0.8693
Refinement method	Full-matrix least-	Full-matrix least-
	squares on F^2	squares on F^2
Data/restraints/parameters	8756/0/461	8062/0/551
Goodness-of-fit on F^2	1.037	1.019
Final <i>R</i> indices $[F^2 > 4\sigma(F^2)]$	$R_1 = 0.0277,$	$R_1 = 0.0590,$
	$wR_2 = 0.0703$	$wR_2 = 0.1083$
R indices (all data)	$R_1 = 0.0328,$	$R_1 = 0.1097,$
	$wR_2 = 0.0730$	$wR_2 = 0.1260$
Extinction coefficient	0.0029(5)	
Largest difference in peak and hole (e \mathring{A}^{-3})	0.489 and -0.390	0.738 and -0.564

Table 5

Ni(1) - S(1)

 $C_{14}H_{12}N_2\cdot C_6H_6$

3.3. Crystal structure determination

A translucent green, block crystal of Ni[S₂P(OC₆H₄Mep)₂]₂ · C₁₀H₈N₂ (**6**) and a green prism crystal of Ni[S₂-P(OC₆H₄Me-o)₂] · C₁₄H₁₂N₂ · C₆H₆ (**7**) were mounted on a glass fibre. Data were collected on a Bruker-Nonius Kappa CCD area detector diffractometer, with ϕ and ω scans chosen to give a complete asymmetric unit. Cell refinement [33] gave cell constants corresponding to a triclinic cell for **6** and a monoclinic cell for **7** whose dimensions are given in Table 3 along with other experimental parameters. The crystal of **7** was a monoclinic pseudo merohedral twin with beta approximately 90° emulating orthorhombic. An absorption correction was applied [34].

The structures were solved by direct methods [35] and refined using the WinGX version [36] of SHELX-97 [37]. All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final

Table 4				
Bond lengths (Å)	and angles (°)	for Ni[S ₂ P(O	$C_6H_4Me-p_2$	$C_{10}H_8N_2$

Ni(1)-S(1)	2.4757(7)	Ni(1)-S(3)	2.4814(7
Ni(1)-S(2)	2.5049(4)	Ni(1)-S(4)	2.5096(6
Ni(1) - N(1)	2.060(1)	Ni(1) - N(2)	2.079(1)
S(1) - P(1)	1.9788(5)	S(3) - P(2)	1.9727(6
S(2) - P(1)	1.9751(6)	S(4) - P(2)	1.9645(6
P(1)–O(1)	1.602(1)	P(2)–O(3)	1.609(1)
P(1)–O(2)	1.604(1)	P(2)–O(4)	1.605(1)
O(1)–C(1)	1.406(2)	O(3)–C(15)	1.404(2)
O(2)–C(8)	1.406(2)	O(4)–C(22)	1.401(2)
N(1)-C(29)	1.352(2)	N(2)-C(34)	1.351(2)
N(1)-C(33)	1.340(2)	N(2)-C(38)	1.339(2)
S(1)-Ni(1)-S(2)	81.33(2)	S(3)-Ni(1)-S(4)	81.99(2)
S(1)-Ni(1)-S(3)	173.09(2)	S(1)-Ni(1)-S(4)	93.46(2)
S(2)-Ni(1)-S(3)	93.53(2)	S(2)-Ni(1)-S(4)	91.33(2)
N(1)-Ni(1)-N(2)	79.10(5)		
N(1)–Ni(1)–S(1)	92.73(4)	N(2)-Ni(1)-S(1)	88.41(4)
N(1)–Ni(1)–S(2)	95.17(4)	N(2)-Ni(1)-S(2)	168.03(4)
N(1)-Ni(1)-S(3)	92.33(4)	N(2)-Ni(1)-S(3)	97.18(4)
N(1)-Ni(1)-S(4)	171.63(4)	N(2)-Ni(1)-S(4)	95.45(4)
P(1)-S(1)-Ni(1)	84.50(2)	P(2)-S(3)-Ni(1)	81.71(2)
P(1)-S(2)-Ni(1)	83.79(2)	P(2)-S(4)-Ni(1)	81.13(2)
C(33)–N(1)–Ni(1)	126.2(1)	C(38)–N(2)–Ni(1)	126.6(1)
C(29)-N(1)-Ni(1)	115.1(1)	C(34)-N(2)-Ni(1)	114.1(1)
O(1)–P(1)–O(2)	92.19(6)	O(3)–P(2)–O(4)	97.02(6)
S(1)-P(1)-S(2)	110.34(2)	S(3)-P(2)-S(4)	112.53(3)
O(1) - P(1) - S(1)	112.77(5)	O(3) - P(2) - S(3)	112.20(5)
O(1)–P(1)–S(2)	113.46(5)	O(3) - P(2) - S(4)	114.10(5)
O(2) - P(1) - S(1)	113.25(5)	O(4) - P(2) - S(3)	107.01(4
O(2) - P(1) - S(2)	113.84(5)	O(4) - P(2) - S(4)	112.81(5
C(1)-O(1)-P(1)	121.48(9)	C(15)–O(3)–P(2)	125.33(9)
C(8)-O(2)-P(1)	123.38(9)	C(22)-O(4)-P(2)	125.19(9)
C(6)–C(1)–O(1)	118.7(1)	C(20)-C(15)-O(3)	118.0(4)
C(2)-C(1)-O(1)	119.5(1)	C(16)-C(15)-O(3)	119.9(1)
C(13)-C(8)-O(2)	119.4(1)	C(27)-C(22)-O(4)	123.1(1)
C(9)-C(8)-O(2)	119.0(1)	C(23)-C(22)-O(4)	116.0(1)
C(33)-N(1)-C(29)	118.7(1)	C(38)-N(2)-C(34)	118.4(1)
N(1)-C(29)-C(30)	121.5(1)	N(2)-C(34)-C(35)	121.9(2)
N(1)-C(29)-C(34)	115.1(1)	N(2)-C(34)-C(29)	115.4(1)
N(1)-C(33)-C(32)	122.7(2)	N(2)-C(38)-C(37)	122.5(2)

Ni(1)-S(2)2.539(1) $Ni(1) \cdot \cdot \cdot S(4)$ 5.462(2)Ni(1) - N(1)2.010(4)Ni(1) - N(2)2.009(5)S(1) - P(1)1.997(2)S(3) - P(2)1.995(2) S(4) - P(2)S(2) - P(1)1.969(2)1.941(2)P(1) - O(1)1.604(4)P(2) - O(3)1.607(4)1.596(4) P(1) - O(2)P(2) - O(4)1.610(4)O(1) - C(1)1.437(7)O(3) - C(15)1.411(8) 1.401(7)O(4)-C(22) 1.385(8) O(2) - C(8)N(1)-C(29)1.363(7)N(2)-C(35)1.366(7)N(1)-C(33) 1.325(7) N(2)-C(41)1.330(7)S(1)-Ni(1)-S(2)82.05(4) N(1)-Ni(1)-N(2)82.6(2)N(1)-Ni(1)-S(1) S(1)-Ni(1)-S(3)134.3(1) 85.17(5) N(2)-Ni(1)-S(1)142.1(1)S(2)-Ni(1)-S(3)167.05(5) N(1)-Ni(1)-S(2)89.9(1) N(1)-Ni(1)-S(3)100.6(1)N(2)-Ni(1)-S(2)91.6(1) N(2)-Ni(1)-S(3)97.3(1)P(1)-S(1)-Ni(1)87.06(6) P(2)-S(3)-Ni(1)113.28(7) P(1)-S(2)-Ni(1)82.60(6) S(1) - P(1) - S(2)108.27(8)S(3) - P(2) - S(4)116.1(1)O(1) - P(1) - S(1)O(3) - P(2) - S(3)111.0(2)113.0(2)O(2) - P(1) - S(1)112.7(2)O(4) - P(2) - S(3)105.2(2)O(1)-P(1)-S(2)114.2(2)O(3)-P(2)-S(4) 112.8(2) O(2) - P(1) - S(2)114.8(2)O(4) - P(2) - S(4)113.2(2)O(1) - P(1) - O(2)93.6(2) O(3) - P(2) - O(4)96.5(2) C(1) - O(1) - P(1)120.9(3)C(15)-O(3)-P(2)127.6(4)C(8)-O(2)-P(1) 122.4(3) C(22)-O(4)-P(2) 125.0(4) C(2)-C(1)-O(1)119.9(6) C(16)-C(15)-O(3)116.8(6) C(6)-C(1)-O(1)116.4(5)C(20)-C(15)-O(3)119.5(6) C(9)-C(8)-O(2) 119.8(6) C(23)-C(22)-O(4)120.9(7)C(29)-N(1)-Ni(1) 112.2(4)C(35)-N(2)-Ni(1) 112.0(4) 129.2(4) C(33)-N(1)-Ni(1)128.1(4)C(41)-N(2)-Ni(1)C(29)-N(1)-C(31)119.7(5) C(35)-N(2)-C(41)118.9(5)

Bond lengths (Å) and angles (°) for $Ni[S_2P(OC_6H_4Me-o)_2]_2$.

Ni(1) - S(3)

2.352(1)

cycle of full-matrix least-squares refinement was based on 8756 observed reflections (7822 for $F^2 > 4\sigma(F^2)$) and 461 variable parameters for **6** and 8062 observed reflections (5543 for $F^2 > 4\sigma(F^2)$); and 551 variable parameters for **7** and converged (largest parameter shift was 0.001 times its esd).

N(2)-C(35)-C(29)

N(2)-C(35)-C(36)

N(2)-C(41)-C(40)

N(2)-C(41)-C(42)

116.4(5)

122.6(6)

120.4(5)

118.6(5)

Selected distances and bond angles are given in Tables 4 and 5 for molecules 6 and 7, respectively and the molecules are displayed as ORTEP diagrams in Figs. 1 and 2.

4. Concluding comments

N(1)-C(29)-C(35)

N(1)-C(29)-C(30)

N(1)-C(33)-C(32)

N(1)-C(33)-C(34)

We have successfully prepared and characterized the following complexes, Ni[S₂P(OR)₂]₂ · *n*L ((R = *o*-, *m*-, *p*-C₆H₄Me; *n* = 2, L = C₅H₅N; *n* = 1, L = C₁₀H₈N₂, C₁₄H₁₂N₂). The IR, UV-visible and magnetic measurements of all of these nickel adducts and molecular structures of two representative complexes, Ni[S₂-P(OC₆H₄Me-*p*)₂]₂ · C₁₀H₈N₂ and Ni[S₂P(OC₆H₄Me-*o*)₂]₂ · C₁₄H₁₂N₂ · C₆H₆ suggest the distorted octahedral for complexes **1**-**6** and distorted trigonal bipyramidal environ-

2.386(1)

116.8(5)

123.8(5)

120.6(6)

117.1(5)

ments around nickel for complexes 7–9 and are consistent with the proposed structures for the analogous complexes $Ni[S_2P(OMe)_2]_2 \cdot phen$, $Ni[S_2P(OMe)_2]_2 \cdot dmphen$ and $Ni[S_2POCMe_2CMe_2O)_2]_2 \cdot dmphen$.

Acknowledgements

One of us (M.N.) is grateful to CSIR, New Delhi for financial support and Department of Chemistry, University of Southampton for spectroscopic facilities. M.B.H. thanks EPSRC for support of the X-ray facilities at Southampton University. J.E.D. wishes to thank the University of Windsor for financial support.

Appendix A. Supplementary material

CCDC 630576 and 630577 contain the supplementary crystallographic data for Ni[S₂P(OC₆H₄Me-p)₂]₂ · C₁₀H₈ N₂ and Ni[S₂P(OC₆H₄Me-o)₂]₂ · C₁₄H₁₂N₂ · C₆H₆. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit @ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2007.01.003.

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