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trans-Bis[*O*-2,4-di-*tert*-butylphenyl (4-methoxyphenyl)dithiophosphonato-κ^2S,S']nickel(II)

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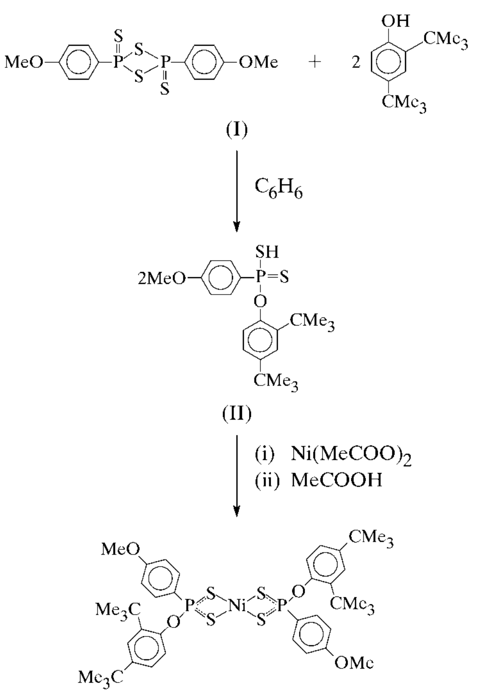
In the the title compound, [Ni($C_{21}H_{28}O_2PS_2$)$_2$], the Ni atom resides on an inversion centre and is coordinated in a square-planar array by four S atoms, with Ni—S and P—S bond lengths of 2.2336 (12)/2.2351 (13) and 1.9910 (16)/2.0010 (17) Å, respectively. The two *O*-2,4-di-*tert*-butylphenyl and two 4-methoxyphenyl moieties adopt *trans* configurations about the central Ni atom.

Comment

Owing to their insecticide and antioxidant activities, dithiophosphonate compounds have been widely investigated in the fields of medicine, industry and agriculture. Despite this, studies on the molecular structures of dithiophosphonate complexes have not been reported adequately up until recently. In recent years, Ni^{II} complexes of this type have received increasing attention owing to their extensive applications as both antioxidants and antiwear additives in the rubber industry and in lubrication engineering (Harrison & Kikabhai, 1987; Kovtun *et al.*, 1992). Additionally, the adducts and their products are also useful in biological applications (Hao, Fun *et al.*, 2001). Consequently, the synthesis, physicochemical investigations and crystal structures of many similar complexes and their adducts have been reported (You *et al.*, 1994; Huang *et al.*, 1995; Hao, Fun *et al.*, 2001; Hao, Jian *et al.*, 2001). A previous study involving a related Ni^{II}–dithiophosphonate complex, namely *trans*-bis[*O*-*n*-propyl (*p*-methoxyphenyl)dithiophosphonato]nickel(II), has been reported (Özcan *et al.*, 2002). The title complex, (III), was prepared and the structure determined in an extension of our previous research studies.

The Ni atom lies on a crystallographic centre of symmetry and the asymmetric unit consists of half of the nickel(II) complex molecule (Fig. 1). The Ni atom is coordinated by four S atoms and has a *trans* configuration imposed by the ligands in a square-planar environment. The dihedral angle between the S—Ni—S coordination planes is 88.70 (5)°, and the Ni—S and S—P bond lengths are 2.2336 (12)/2.2351 (13) and 1.9910 (16)/2.0010 (17) Å, respectively. These bond lengths compare well with those found in other related Ni^{II} complexes (Haiduc *et al.*, 1984; Hoskins & Tiekink, 1985; Arca *et al.*, 1997; van Zyl *et al.*, 1998; Hao, Fun *et al.*, 2001; Hao, Jian *et al.*, 2001; Özcan *et al.*, 2002).



The differences in the Ni—S and S—P bond lengths are comparable with those found in our previous study (Özcan *et al.*, 2002), where the values were 2.2251 (9)/2.2283 (9) and 2.004 (1)/2.008 (1) Å, respectively. These differences were explained by electron delocalization in the P—S π-bonding in

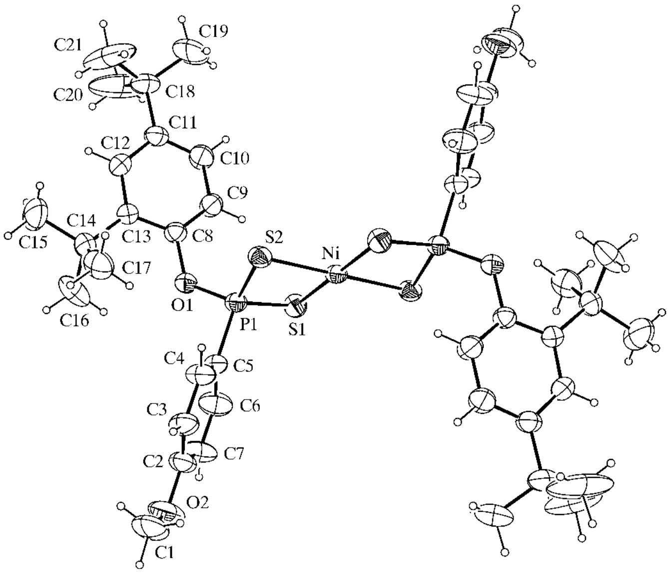


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of (III), showing the atom-numbering scheme and ellipsoids at the 40% probability level.

our previous work. Similar observations have also been made in the present and related studies (Ooi & Fernando, 1968; Arora *et al.*, 1978; Hoffmann *et al.*, 1979; Hoskins & Tiekink, 1985; Hao, Fun *et al.*, 2001; Hao, Jian *et al.*, 2001). Small differences in the geometric parameters around the central Ni atom may also be explained by the steric effect of different molecular groups attached to the P atom in related complexes. The mean Ni—S—P angle in (III) (Table 1) is in good agreement with similar angles found in bis(butyldithiophosphato)bis(4-aminopyridine)nickel(II) [82.83 (5)°; You *et al.*, 1994] and [Ni{$(C_4H_9O)_2PS_2$}(pyridine)$_2$] [82.57°; Liu *et al.*, 1987]. The C—O distance in the *O*-2,4-di-*tert*-butylphenyl (O-dtb) group is much longer than the range found in bis(di-*p*-tolyldithiophosphato)(1,10-phenanthroline)nickel(II) [1.398 (4)–1.47 (1) Å; Hao, Fun *et al.*, 2001] and is probably the result of electronic effects from the aromatic ring. All other structural parameters have normal values. The methoxyphenyl group and the main part of the O-dtb group (atoms O1, C8–C14 and C18) are individually planar and the dihedral angle between these planes is 62.6 (1)°.

Experimental

Lawesson's reagent, (I) (1.48 g, 3.53 mmol), was treated with 2,4-di-*tert*-butylphenol (1.45 g, 7.07 mmol) in hot benzene (25 ml), yielding the *O*-di-*tert*-butylphenyl ester of dithiophosphonic acid, (II). The title compound, (III), was prepared by the reaction of (II) with nickel(II) acetate in a 1:1 mixture of benzene and acetic acid. The compound crystallizes directly from the reaction medium and these crystals were used for the X-ray study. The purple-coloured compound (III) melts at 515–516 K, is stable well over its melting point, and recrystallizes, upon cooling, just below the melting temperature without any observable change in its colour. IR (KBr, cm^{-1}): 552 (PS, symmetric), 670 (PS, asymmetric); 1028 (POC).

Crystal data

[Ni$(C_{21}H_{28}O_2PS_2)_2$]
M_r = 873.76
Monoclinic, $P2_1/c$
a = 8.1782 (18) Å
b = 32.060 (12) Å
c = 8.709 (3) Å
β = 94.68 (3)°
V = 2275.8 (12) Å^3
Z = 2
D_x = 1.275 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4916 reflections
θ = 9.9–18.0°
μ = 0.72 mm^{-1}
T = 293 (2) K
Prism, violet
0.30 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.814, $T_{\max}$ = 0.870
4916 measured reflections
4611 independent reflections
2618 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.045
$\theta_{\max}$ = 26.3°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 39$
$l = -10 \rightarrow 0$
4916 standard reflections
frequency: 120 min
intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.141
S = 0.99
4611 reflections
241 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2 + 0.9574P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.53 e Å^{-3}
$\Delta\rho_{\min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—S2	2.2336 (12)	P1—S2	1.9910 (16)
Ni—S1	2.2351 (13)	P1—S1	2.0010 (17)
Ni—P1	2.7942 (14)	O1—C8	1.423 (5)
P1—O1	1.598 (3)		
S2—Ni—S1	88.70 (5)	O1—P1—C5	100.53 (18)
S2—P1—S1	102.98 (7)	O1—P1—S2	113.63 (13)
P1—S1—Ni	82.34 (6)	C5—P1—S1	112.16 (16)
P1—S2—Ni	82.60 (6)		

H atoms bonded to C atoms were placed geometrically and all H atoms were treated as riding, with C—H distances of 0.93 and 0.96 Å, and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1114). Services for accessing these data are described at the back of the journal.

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