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trans-Bis(2-aminopyridine-*N*)bis(*O*,*O*′-diisopropyl dithiophosphato-*S*,*S*′)-nickel(II)

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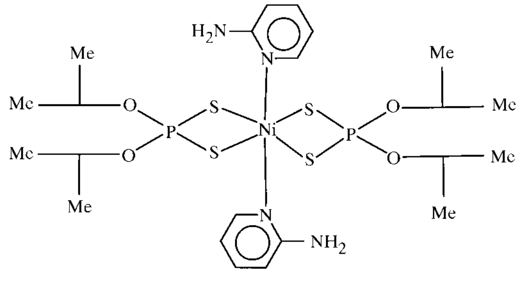
In the title compound, $[Ni(C_6H_{14}O_2PS_2)_2(C_5H_6N_2)_2]$, the coordination around the Ni atom, which lies on a crystallographic centre of symmetry, is octahedral with the S atoms from the dithiophosphate ligands occupying the equatorial positions, while the axial positions are occupied by the ring N atoms of the 2-aminopyridine ligands. The molecules form layers in the *bc* plane which are stacked in the direction of the *a* axis.

Comment

Nickel(II) dialkyl dithiophosphates and their derivatives find wide applications in rubber chemistry and technology, and as lubrication oil additives (Jones & Symes, 1971). Metal chelates in which the metal ion is coordinately unsaturated can act as electron acceptors and yield adducts with neutral molecules which are electron donors (Harrison *et al.*, 1986). Adducts and their formation reactions have also been found useful in a variety of ways. In recent years, adducts of nickel(II) dialkyl dithiophosphate with neutral nitrogen bases have received increasing attention, partly because of the reactivity of a variety of nitrogen bases with nickel(II) dialkyl dithiophosphate in solution (Liu *et al.*, 1991; You *et al.*, 1994; Xiong *et al.*, 1995). The antioxidant effectiveness for diisopropyl dithiophosphates decreases in the order: Co > Ni > Zn > Cu > Cd > Ba = Ca. For Ni dialkyl dithiophosphates, the effectiveness decreases in the order ^{i}Pr > cyclohexyl > ^{t}Bu (Kovtun *et al.*, 1992). Furthermore, the amines in lubricating oil have a great influence on the properties of metal dialkyl dithiophosphate additives (Shiomi *et al.*, 1989).



(I)

The Ni atom in the title compound, (I) (Fig. 1), lies on a crystallographic centre of symmetry with the dithiophosphate (dtp) ligands coordinated to it by their two S atoms, forming four-membered chelate rings. The two 2-aminopyridine molecules are coordinated to the central Ni atom through the two ring N atoms. This coordination forms a distorted octahedral environment around Ni with S1, S1($2 - x$, $1 - y$, $-z$), S2 and S2($2 - x$, $1 - y$, $-z$) at the equatorial positions, while the axial positions are occupied by the 2-aminopyridine moieties. The ideal octahedral geometry is distorted by the minor steric constraints imposed by the restricted bite angles of the dithiophosphate ligand.

The S1—Ni1—S2 and S1—P1—S2 bond angles, and Ni—S bond lengths are comparable with those of $Ni[(C_2H_5O)_2PS_2]_2py_2$ [81.7 (1), 110.4 (3)° and 2.49 (1)–2.50 (1) Å, respectively; Ooi & Fernando, 1967] and $Ni[(C_4H_9O)_2PS_2]_2py_2$ [81.5 (1), 111.7 (1)° and 2.486 (1)–2.511 (1) Å, respectively; Liu *et al.*, 1987], whereas the Ni—N bond lengths are about 0.11 Å longer than those in these two related compounds [2.11 (1) and 2.116 (4) Å, respectively]. However, the S1—Ni1—S2 and S1—P1—S2 bond angles are slightly smaller than those found in $[Ni(Bu\text{-}dtp)_2(4\text{-}amino\text{-}py)_2]$ [81.91 (5) and 112.46 (5)°, respectively; You *et al.*, 1994]. The mean Ni—S bond length in the title compound is substantially longer than the value of 2.222 (1) Å reported for $Ni[(C_3H_7O_2)_2PS_2]_2$ (Hoskins & Tiekink, 1985). This is a direct consequence of the six- *versus* four-coordinate electronic

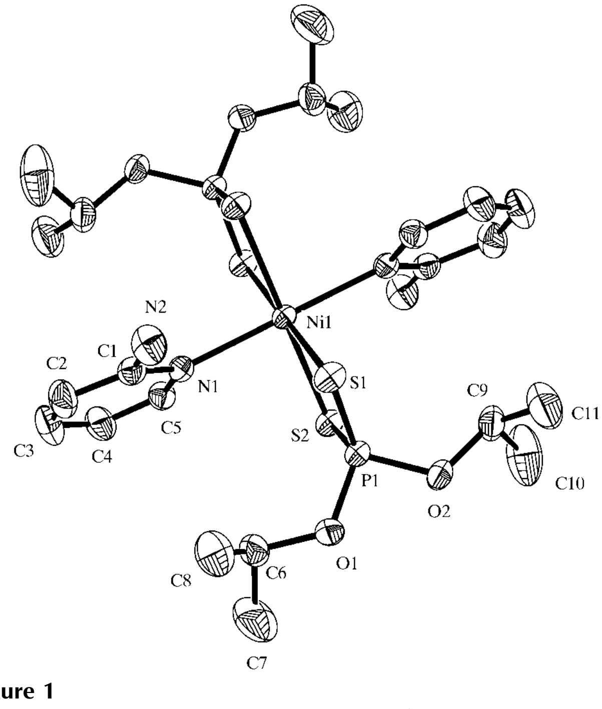


Figure 1
The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

environments of the metal centres in the two compounds. The mean Ni—S—P angle in the title complex is larger than those of [Ni(Bu-dtp)$_2$(4-aminopy)$_2$] [82.83 (5)°; You *et al.*, 1994] and Ni[(C$_4$H$_9$O)$_2$PS$_2$]$_2$py$_2$ (82.57°; Liu *et al.*, 1987). However, this angle is comparable to the mean value of 85.08 (6)° reported by Hoskins & Tiekink (1985).

The P—S bond lengths are comparable to those in Ni-[(C$_3$H$_7$O$_2$)$_2$PS$_2$]$_2$ [1.991 (2) and 1.993 (2) Å; Hoskins & Tiekink, 1985], but different from those in Zn[(^{i}PrO)$_2$PS$_2$]$_2$-(bipy) [2.005 (6), 1.925 (6), 1.997 (8) and 1.926 (9) Å; Harrison *et al.*, 1986], where the S atoms of the shorter bonds are not bonded to or are only very weakly interacting with the central atom. The P—O, O—C and C—C bond lengths of the bis(*O*,*O*′-disopropyl dithiophosphate) are comparable with the reported values (Hoskins & Tiekink, 1985).

In the crystal, the molecules are arranged in layers in the *bc* plane. Layers are stacked in the *a*-axis direction by S2$\cdots$S2($1 - x$, $1 - y$, $-z$) interactions [3.5475 (6) Å].

Experimental

The title compound was prepared by adding nickel(II) bis(*O*,*O*′-diisopropyl dithiophosphate) (0.01 mmol) to EtOH (80 ml) followed by the addition of 2-aminopyridine (0.02 mmol). The mixture was heated until the solids dissolved and was then filtered. The filtrate was allowed to stand at room temperature. Dark-green crystals formed upon slow evaporation of the solvent.

Crystal data

[Ni(C$_6$H$_{14}$O$_2$PS$_2$)$_2$(C$_5$H$_6$N$_2$)$_2$]
M_r = 673.47
Monoclinic, $P2_1/n$
a = 6.6296 (1) Å
b = 16.3605 (2) Å
c = 14.6386 (2) Å
β = 99.938 (1)°
V = 1563.93 (4) Å^3
Z = 2
D_x = 1.430 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
θ = 2.49–28.34°
μ = 1.024 mm^{-1}
T = 293 (2) K
Slab, dark green
0.40 × 0.24 × 0.14 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.685, $T_{\max}$ = 0.870
10833 measured reflections
3823 independent reflections
3246 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.058
$\theta_{\max}$ = 28.28°
$h = -8 \rightarrow 8$
$k = -21 \rightarrow 20$
$l = -19 \rightarrow 10$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.087
S = 0.97
3823 reflections
169 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0410P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.43 e Å^{-3}
$\Delta\rho_{\min}$ = −0.71 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	2.2275 (14)	P1—S1	1.9866 (6)
Ni1—S2	2.4865 (4)	P1—S2	1.9879 (6)
Ni1—S1	2.5123 (4)	O1—C6	1.464 (2)
P1—O1	1.5863 (14)	O2—C9	1.464 (2)
P1—O2	1.5892 (12)		
N1—Ni1—S2	88.41 (4)	S1—P1—S2	109.44 (3)
N1—Ni1—S1	92.10 (4)	P1—S1—Ni1	84.476 (19)
S2—Ni1—S1	80.940 (14)	P1—S2—Ni1	85.142 (19)

After checking their presence in the difference map, the positions of all H atoms were geometrically calculated and allowed to ride on their attached atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1110). Services for accessing these data are described at the back of the journal.

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