

## Bis(di-*tert*-butylthiophosphinic isopropylamidato-*N,S*)nickel(II)

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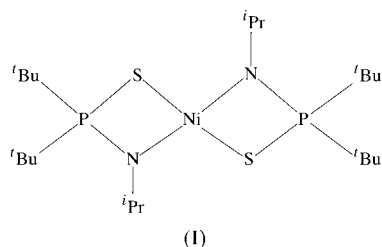
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The crystal structure of the title compound,  $[\text{Bu}_2\text{P}(\text{S})\text{N}^i\text{Pr}]_2\text{Ni}$  or  $[\text{Ni}(\text{C}_{11}\text{H}_{25}\text{NPS})_2]$ , shows a dihedral angle of  $82.27(6)^\circ$  between the two Ni/S/N planes and thus a distorted tetrahedral arrangement of the  $\text{NiN}_2\text{S}_2$  chromophore. The structure is in accordance with the observed paramagnetism and is contrasted with the oxo analogue, which is planar but also paramagnetic.

### Comment

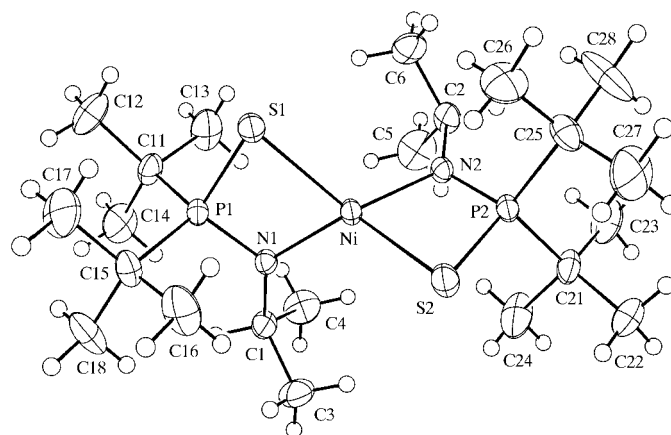
Tetracoordinate  $\text{Ni}^{\text{II}}$  complexes  $[\text{R}_2\text{P}(\text{X})\text{NR}']_2\text{Ni}$  ( $\text{X} = \text{O}, \text{S}$ ) are either planar or (distorted) tetrahedral. Diamagnetism and a lack of ligand-field bands below  $10\,000\text{ cm}^{-1}$  in solution on the one hand, and paramagnetism on the other hand, had been regarded as safe criteria for the assignment of planar and tetrahedral coordination geometries, respectively. However, the first exceptions from this rule were found recently with several phosphinic amidato bis-chelates,  $[\text{R}_2\text{P}(\text{O})\text{NR}']_2\text{Ni}$ . Solid  $[\text{Bu}_2\text{P}(\text{O})\text{N}^i\text{Pr}]_2\text{Ni}$ , the oxo analogue of the title complex, (I), is paramagnetic [ $\mu_{\text{eff}} = 3.4\text{ BM}$  (or  $\mu_{\text{B}}$ ) at  $297\text{ K}$ ] and shows a strong absorption at  $7300\text{ cm}^{-1}$ . Nevertheless, the crystal structure revealed an exactly planar  $\text{NiN}_2\text{O}_2$  chromophore (Frömmel, Peters *et al.*, 1992).



The title compound, (I), is also paramagnetic ( $\mu_{\text{eff}} = 3.32\text{ BM}$  at  $295\text{ K}$ ) and shows an absorption at  $6300\text{ cm}^{-1}$  in toluene. Based on these data, a tetrahedral structure had been postulated [for preparation and physical measurements *cf.* Deeg *et al.* (1991)]. The results of the oxo analogue prompted us to check this postulation with regard to the current crystal structure, preliminary results of which have been published

elsewhere (Frömmel, Kuchen *et al.*, 1992; Frömmel, Peters *et al.*, 1992; Wunderlich, 1996).

The Ni—S—P—N chelate rings are irregular quadrangles with average bond lengths of Ni—S 2.383 (1), S—P 2.009 (1), P—N 1.610 (2) and N—Ni 1.941 (2) Å, and average endocyclic angles of  $80.49(6)$  (bite angle at Ni),  $76.96(3)$  (at S),  $101.49(7)$  (at P) and  $101.0(1)^\circ$  (at N) (*cf.* Table 1). Both rings are planar to within 0.02 Å. The oxo analogue (Frömmel, Peters *et al.*, 1992) is planar to within 0.005 Å and reveals, as expected, shorter distances to the chalcogen atom [Ni—O 2.103 (2) and O—P 1.517 (2) Å] and also a reduced Ni—N bond length of 1.903 (2) Å. The angles O—Ni—N of  $74.2(1)^\circ$  and Ni—N—P of  $94.5(1)^\circ$  are smaller, while the Ni—O—P angle of  $89.6(1)^\circ$  is larger than the corresponding angles of the present thio complex.



**Figure 1**

The crystal structure of (I) shown with 25% probability displacement ellipsoids. H atoms are displayed as circles with a radius of 0.15 Å. The *tert*-butyl groups show high displacement parameters ( $U_{11}$  up to  $0.27\text{ Å}^2$ ).

The main differences between the two complexes are associated with the coordination of the Ni atom. The current structure reveals a dihedral angle at the Ni atom within the chromophore of  $82.27(6)^\circ$  and thus a slightly distorted tetrahedral coordination in accordance with the measured paramagnetism. Because of its  $\bar{1}$  point symmetry, the oxo analogue is exactly planar, a fact that contradicts the observed paramagnetism. But analogous results have been reported for the planar and tetrahedral isomers of  $[\text{Bu}_2\text{P}(\text{O})\text{NCy}]_2\text{Ni}$  (Cy is cyclohexyl; Frömmel *et al.*, 1993).

We conclude that the magnetic and spectroscopic criteria for the assignment of the coordination geometry are still valid in the case of thio compounds. How far  $R$ ,  $R'$ ,  $X$  and possible packing effects influence the existence of paramagnetic planar  $\text{Ni}^{\text{II}}$ -oxo complexes has been discussed by Brück *et al.* (1996), and in the literature cited therein.

### Experimental

Details of the synthesis of the title compound are given in Deeg *et al.* (1991).

## Crystal data

[Ni(C <sub>11</sub> H <sub>25</sub> NPS) <sub>2</sub> ]	$D_x = 1.176 \text{ Mg m}^{-3}$
$M_r = 527.41$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 32 reflections
$a = 16.123 (2) \text{ \AA}$	$\theta = 14.1\text{--}17.0^\circ$
$b = 11.684 (1) \text{ \AA}$	$\mu = 0.910 \text{ mm}^{-1}$
$c = 15.815 (2) \text{ \AA}$	$T = 300 (2) \text{ K}$
$\beta = 90.74 (1)^\circ$	Polyhedron, intense metallic blue
$V = 2979.0 (6) \text{ \AA}^3$	$0.50 \times 0.45 \times 0.45 \text{ mm}$
$Z = 4$	

## Data collection

Siemens/Bruker P3 diffractometer	$h = -20 \rightarrow 20$
$\omega$ -2 $\theta$ scans	$k = -15 \rightarrow 0$
6844 measured reflections	$l = 0 \rightarrow 20$
6844 independent reflections	3 standard reflections
4889 reflections with $I > 2\sigma(I)$	every 100 reflections
$\theta_{\text{max}} = 27.56^\circ$	intensity decay: 14%

## Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = [\sigma^2(F_o^2) + (0.0723P)^2]$
$wR(F^2) = 0.116$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.000$	$(\Delta/\sigma)_{\text{max}} < 0.001$
6844 reflections	$\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$
263 parameters	$\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$

Methyl and methine H atoms were calculated as staggered and were refined in riding mode (C—H = 0.96 and 0.98 Å, respectively).

Data collection: P3 (Siemens, 1989); cell refinement: P3; data reduction: SHELXTL-Plus (Sheldrick, 1990); program(s) used to solve structure: SHELXTL-Plus; program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-Plus; software used to prepare material for publication: SHELXL97.

Table 1

Selected geometric parameters (Å, °).

Ni—N1	1.9397 (18)	S1—P1	2.0109 (9)
Ni—N2	1.9419 (19)	S2—P2	2.0067 (10)
Ni—S2	2.3814 (8)	P1—N1	1.6126 (19)
Ni—S1	2.3839 (8)	P2—N2	1.608 (2)
N1—Ni—N2	138.48 (8)	P1—S1—Ni	76.75 (3)
N1—Ni—S2	121.59 (6)	P2—S2—Ni	77.16 (3)
N2—Ni—S2	80.24 (6)	N1—P1—S1	101.68 (7)
N1—Ni—S1	80.74 (6)	N2—P2—S2	101.29 (7)
N2—Ni—S1	119.90 (6)	P1—N1—Ni	100.74 (9)
S2—Ni—S1	121.56 (3)	P2—N2—Ni	101.25 (10)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1401). Services for accessing these data are described at the back of the journal.

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