

Bis(*O,O'*-di-*p*-tolyl)dithiophosphato-*S,S'*-(1,10-phenanthroline-*N,N'*)-nickel(II)

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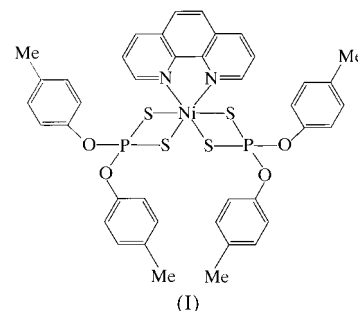
The title coordination complex, $[\text{Ni}(\text{C}_{14}\text{H}_{14}\text{O}_2\text{PS}_2)_2(\text{C}_{12}\text{H}_8\text{N}_2)]$ or $[\text{Ni}(p\text{MePh-dtp})_2(\text{phen})]$ (phen is 1,10-phenanthroline; dtp is diaryldithiophosphate), has a non-crystallographic twofold axis of symmetry through the Ni atom and the phen moiety. Two *O,O'*-di-*p*-tolyl dithiophosphate (dtp) ions act as bidentate ligands. The central metal atom is coordinated by four S atoms from two dtp groups and two N atoms from the phen ligand. The title compound displays distorted octahedral geometry around the central Ni atom.

Comment

In recent years, adducts of nickel(II) dithiophosphate with neutral nitrogen ligands 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 formation reactions have also been found useful in a variety of ways, such as in biological applications and as both ultraviolet absorbers and antioxidants. In addition to their syntheses and various physicochemical investigations, the crystal structures of many nickel(II) complexes and their adducts with nitrogen bases have been reported (Huang *et al.*, 1995; You *et al.*, 1994). Metal complexes of the $[M(LL)_3]$ ion type, where *LL* is either 1,10-phenanthroline (phen) or a modified phen ligand, are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA (Barton, 1986; Naing *et al.*, 1995). Thus, the crystal structure of $[\text{Ni}(p\text{MePh-dtp})_2(\text{phen})]$, (I), was determined.

A perspective view of the title complex with the atomic numbering scheme is shown in Fig. 1. In the title complex, the Ni^{II} atom lies in the centre of the octahedral geometry of the

NiN_2S_4 chromophore. Crystals of this compound are composed of discrete molecules.



The Ni—S distances of the title complex (Table 1) are in good agreement with similar distances found in the six-coordinate complex $[\text{Ni}\{(\text{C}_4\text{H}_9\text{O})_2\text{PS}_2\}_2(\text{bipy})]$ [2.466 (2) and 2.524 (2), 2.463 (2) and 2.522 (2) Å; You *et al.*, 1986]. However, the distances are much longer than those in four-coordinate compounds, such as $[\text{Ni}(\text{S}_2\text{COPh-4}'\text{Bu})_2]$ [2.219 (4) and 2.213 (6) Å; Chen & Fackler, 1978], $[\text{Ni}\{(\text{iso-C}_3\text{H}_7\text{O})_2\text{PS}_2\}_2]$ [2.227 (1) and 2.216 (1) Å; Hoskins & Tiekink, 1985] and $[\text{Ni}\{(\text{OC}_2\text{H}_5)(4\text{-CH}_3\text{OPh})\text{PS}_2\}_2]$ [2.1297 (8) and 2.2225 (8) Å; Arca *et al.*, 1997]. This probably reflects the change from octahedral coordination in the title compound to square-planar or tetrahedral coordination.

The Ni—N distances of the title compound (Table 1) are in good agreement with similar distances found in $[\text{Ni}\{(\text{C}_4\text{H}_9\text{O})_2\text{PS}_2\}_2(\text{bipy})]$ [2.089 (4) and 2.088 (4) Å] and $[\text{Ni}\{(\text{C}_2\text{H}_5\text{O})\text{CS}_2\}_2(\text{phen})\cdot 3\text{H}_2\text{O}]$ [2.074 (4) and 2.076 (4) Å; Xiong *et al.*, 1997].

The distances between P1 and the two S atoms (Table 1) are nearly equal. However, the distances between P2 and the other two S atoms are different. It is noteworthy that all the P—S bonds lengths are intermediate between single (2.09 Å)

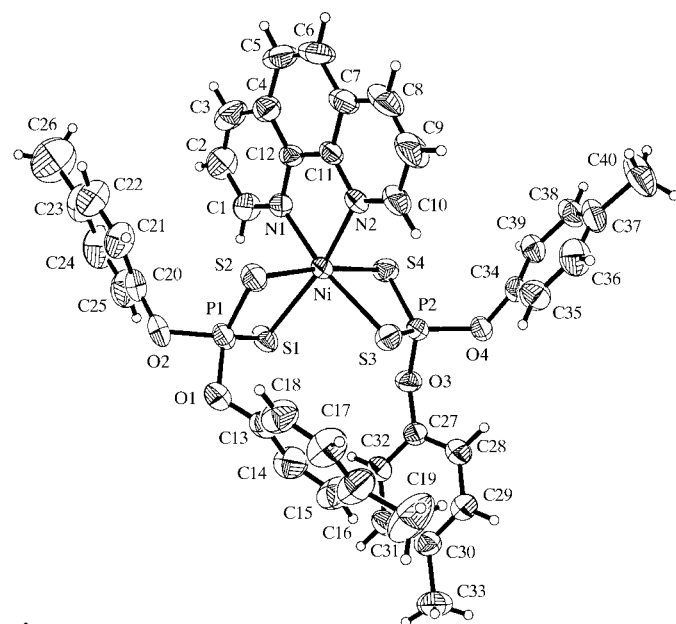


Figure 1

The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

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and the double bond (1.87 Å) values, resulting from substantial delocalization of electrons throughout the two NiS₂P four-membered rings. This is similar to that found for analogous dtp complexes, *e.g.* [Ni{(C₂H₅O)₂PS₂}(C₉H₇N)₂] (Huang *et al.*, 1995), [Ni{(C₄H₉O)₂PS₂}(py)₂] (Liu *et al.*, 1987), [Ni{(C₄H₉O)₂PS₂}(bipy)] and [M₂{(*i*-C₃H₇O)₂PS₂}]₄, M = Zn or Cd (Byrom *et al.*, 2000).

The C—O distances are much shorter than those found in [Ni{(C₂H₅O)₂PS₂}(C₅H₆N₂)₂] [1.446 (5) and 1.430 (5) Å]. This is probably a result of the electronic effect of the benzene rings.

The S—Ni—S bond angles (Table 1) are similar to those found in [Ni{(C₄H₉O)₂PS₂}(bipy)] [81.40 (7) and 81.63 (7)°]. The N1—Ni—N2 bond angle (Table 1) is also similar to that found in [Ni{(C₄H₉O)₂PS₂}(bipy)] [79.5 (2)°].

The phen ligand and Ni atom are also coplanar; the mean deviation from the best plane is 0.065 (1) Å. The two planes through Ni, P and S₂ form a dihedral angle of 89.18 (4) Å. The dihedral angles between the plane of the phen ligand and these two NiS₂P planes are 89.21 (7) and 74.92 (7) Å. This indicates that the structure of NiN₂S₄ is obviously a distorted octahedron.

Experimental

The title compound was prepared by mixing a solution of nickel(II) bis(*O,O'*-di-*p*-tolylidithiophosphate) (0.1 mmol) in acetone (50 ml) and phen (0.1 mmol) with heating. The solution was cooled to room temperature and was then filtered. Green prismatic single crystals suitable for X-ray analysis were obtained upon slow evaporation of the solvent.

Crystal data

[Ni(C₁₄H₁₄O₂PS₂)₂(C₁₂H₈N₂)₂]
M_r = 857.60
 Triclinic, P1
a = 11.1819 (2) Å
b = 12.0934 (2) Å
c = 17.2860 (2) Å
 α = 107.693 (1)°
 β = 96.349 (1)°
 γ = 109.896 (1)°
V = 2033.41 (5) Å³

Z = 2
D_x = 1.401 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 8192 reflections
 θ = 1.3–28.3°
 μ = 0.80 mm⁻¹
T = 293 (2) K
 Prismatic slab, green
 0.40 × 0.24 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
T_{min} = 0.739, *T_{max}* = 0.882
 11 570 measured reflections
 7040 independent reflections

5007 reflections with *I* > 2σ(*I*)
R_{int} = 0.055
 θ_{max} = 25.0°
h = -12 → 13
k = -14 → 11
l = -20 → 19
 Intensity decay: negligible

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.048
wR (*F*²) = 0.120
S = 0.93
 7040 reflections
 482 parameters

H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0346*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.40 e Å⁻³
 Δρ_{min} = -0.77 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni—N1	2.082 (3)	S2—P1	1.977 (1)
Ni—N2	2.086 (3)	S3—P2	1.965 (1)
Ni—S2	2.486 (1)	S4—P2	1.972 (1)
Ni—S4	2.488 (1)	O1—C13	1.417 (4)
Ni—S1	2.505 (1)	O2—C20	1.406 (4)
Ni—S3	2.532 (1)	O3—C27	1.398 (4)
S1—P1	1.976 (1)	O4—C34	1.405 (4)
N1—Ni—N2	79.8 (1)	S1—P1—S2	110.37 (6)
S2—Ni—S1	81.13 (3)	S3—P2—S4	112.81 (5)
S4—Ni—S3	81.57 (3)		

After checking their presence in the difference map, all H atoms were geometrically fixed and allowed to ride on their attached atoms (CH₃ with *AFIX* 137 in *SHELXTL*).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT* and *SADABS* (Sheldrick, 1996); 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 *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1464). Services for accessing these data are described at the back of the journal.

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