

propionate group showed disorder. The occupancies of the disordered positions C23A and C23B were initially refined and then fixed at 0.66 (2) for C23A and 0.34 (2) for C23B. These atoms were isotropically refined with C22—C23A and C22—C23B distances restrained to be equal with an effective standard deviation of 0.02 Å. The H atoms of C22 and C23 (C23A and C23B) were geometrically fixed and allowed to ride on their parent atoms. The remaining H atoms were located from a difference Fourier map and refined isotropically. H atoms belonging to the water molecule could not be located.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXL93 and PARST95 (Nardelli, 1995).

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[1,4-Bis(diphenylphosphino)butane-*P,P'*]- (*N,N'*-diethyldithiocarbamato-*S,S'*)- nickel(II) Perchlorate

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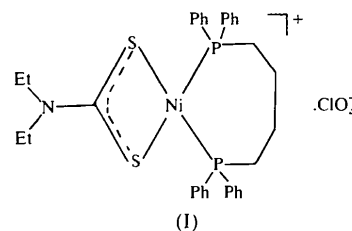
(Received 9 September 1997; accepted 30 January 1998)

Abstract

The title compound, [Ni(C₅H₁₀NS₂)(C₂₈H₂₈P₂)]ClO₄, is planar. The pairs of Ni—S [2.2089 (8) and 2.2075 (8) Å] and Ni—P [2.1945 (7) and 2.1932 (8) Å] bond lengths are respectively equal, and the P—Ni—P angle [95.12 (3)°] is large as a consequence of the flexible butyl chain between the two P atoms. The butyl chain lies on one side of the planar NiS₂P₂ chromophore and two of the phenyl rings are arranged laterally above the plane.

Comment

Since Ni^{II} is a borderline acceptor, its dithiocarbamate complexes show a preferential interaction towards phosphine ligands leading to the formation of NiS₂PCl and NiS₂P₂ chromophores (Venkatachalam *et al.*, 1997). Steric and electronic influences of alkyl substituents on the structures of various nickel dithiocarbamates have been investigated (McCleverty & Morrison, 1976; Lachenal, 1975; Burns *et al.*, 1980). The partial double-bond nature of the thioureide bond in the dithiocarbamate ligands has been correlated with the corresponding IR stretching frequencies (Maxfield, 1970).



The title compound, (I), contains discrete mononuclear [Ni(dedtc)(dppb)]⁺ cations [where dedtc is the S₂CN(C₂H₅)₂⁻ anion and dppb is (C₆H₅)₂PCH₂CH₂-

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CH₂CH₂P(C₆H₅)₂] with no significant intermolecular contacts. Four molecules are present in the unit cell. Atoms Ni, S1, S2, P1 and P2 are coplanar, with deviations from the mean plane of -0.03 , 0.10 , -0.06 , -0.01 and 0.08 Å, respectively. The observed planarity is in keeping with the diamagnetism of the Ni^{II} complex. The Ni—S distances [2.2089(8) and 2.2075(8) Å] are equal and close to those reported for the parent bis-(dithiocarbamate) complex and some of the phosphine-substituted complexes (Bonamico *et al.*, 1965; Manohar *et al.*, 1997). The bite angle of the dithiocarbamate ligand is 78.37(3)° in the present structure, which is close to the value of 78.2(1)° observed in the [Ni(dedtc)(dppe)]⁺ cation, where dppe is (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂ (Ramalingam *et al.*, 1987). The two Ni—P distances [2.1932(8) and 2.1945(7) Å] are also the same in the title complex. The Ni—P distances are longer than those observed in the [Ni(mordtc)(dppe)]⁺ cation, where mordtc is S₂CN(C₅H₁₀) [2.1679(11) and 2.1601(12) Å; Akilan *et al.*, 1995]. Interestingly, the P1—Ni—P2 angle in the present structure [95.12(3)°] is larger than the corresponding angle of 86.81(4)° observed in the [Ni(mordtc)(dppe)]⁺ cation, because of the presence of a flexible butyl chain between the two P atoms. The butyl backbone lies below the plane of the NiS₂P₂ chromophore and exhibits extensive puckering.

The Ni—P distances in the triphenylphosphine analogue of the title compound are 2.200(3) and 2.230(3) Å, and the P—Ni—P angle is 99.7(2)° (Ramalingam *et al.*, 1987). The close similarities observed in the Ni—P distances and P—Ni—P angles between the

title compound and its triphenylphosphine analogue indicate the same degree of freedom of bonding in both complexes.

The thioureide N—C distance is 1.305(4) Å, which compares well with the distance observed in the [Ni(dedtc)(PPh₃)₂]⁺ cation (Ramalingam *et al.*, 1987); there is no significant influence of the chelating phosphine on the thioureide bond.

The bond parameters associated with the phenyl rings are normal. Two of the phenyl rings lie above laterally and two others lie horizontally aligned with the NiS₂P₂ plane.

The perchlorate anion has Cl—O distances in the range 1.373(4)–1.406(3) Å and O—Cl—O angles in the range 104.9(3)–112.1(3)°. Very large displacements are associated with the O atoms, as observed in [Ni(dedtc)(PPh₃)₂](ClO₄) (Ramalingam *et al.*, 1987).

Experimental

Ni(dedtc)₂ and dppb (1:1 ratio) in acetonitrile with the counteranion were refluxed for 1 h. A red product separated on evaporation of the solvent which was recrystallized from CH₂Cl₂ and CH₃OH.

Crystal data

[Ni(C₅H₁₀NS₂)(C₂₈H₂₈P₂)]-
ClO₄
M_r = 732.86
Monoclinic
P2₁/n
a = 18.951(1) Å
b = 9.104(1) Å
c = 20.842(2) Å
β = 100.01(1)°
V = 3541.1(5) Å³
Z = 4
D_x = 1.375 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.71073 Å
Cell parameters from 41
reflections
 θ = 1.75–27.50°
 μ = 0.868 mm⁻¹
T = 293(2) K
Irregular plate
0.86 × 0.62 × 0.36 mm
Red

Data collection

Siemens P4 diffractometer
 $\theta/2\theta$ scans
Absorption correction:
empirical ψ scans
(Siemens, 1994)
T_{min} = 0.521, *T_{max}* = 0.732
9858 measured reflections
8049 independent reflections
5275 reflections with
I > 2 σ (*I*)

R_{int} = 0.020
 θ_{\max} = 27.5°
h = $-1 \rightarrow 24$
k = $-1 \rightarrow 11$
l = $-27 \rightarrow 26$
3 standard reflections
every 97 reflections
intensity decay: <3%

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.044
wR(*F*²) = 0.131
S = 0.945

(Δ/σ)_{max} = 0.001
 $\Delta\rho_{\max}$ = 0.720 e Å⁻³
 $\Delta\rho_{\min}$ = -0.295 e Å⁻³
Extinction correction: none

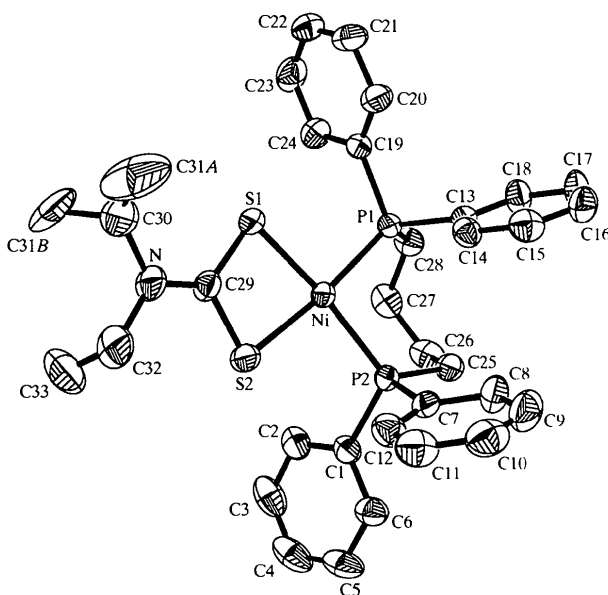


Fig. 1. The molecular structure and atomic numbering of the [Ni(dedtc)(dppb)]⁺ cation (without H atoms). The displacement ellipsoids are drawn at 50% probability.

8049 reflections
518 parameters
H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0808P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Ni—P2	2.1932 (8)	P1—C13	1.819 (3)
Ni—P1	2.1945 (7)	P1—C19	1.821 (3)
Ni—S2	2.2075 (8)	P1—C28	1.852 (3)
Ni—S1	2.2089 (8)	P2—C1	1.816 (3)
Cl—O1	1.373 (4)	P2—C7	1.821 (3)
Cl—O4	1.391 (5)	P2—C25	1.836 (3)
Cl—O2	1.392 (3)	N—C29	1.305 (4)
Cl—O3	1.406 (3)	N—C30	1.475 (5)
S1—C29	1.717 (3)	N—C32	1.490 (5)
S2—C29	1.707 (3)		
P2—Ni—P1	95.12 (3)	C26—C27—C28	115.4 (3)
S2—Ni—S1	78.38 (3)	C27—C28—P1	115.7 (2)
C29—S1—Ni	85.74 (10)	N—C29—S2	123.5 (3)
C29—S2—Ni	86.02 (10)	N—C29—S1	127.2 (2)
C26—C25—P2	115.0 (3)	S2—C29—S1	109.21 (15)
C25—C26—C27	115.1 (3)		

In one of the ethyl substituents of the dithiocarbamate, disorder was observed with respect to the C31 atom; two positions, C31A and C31B, were assigned site occupancies of 0.5. All the H atoms of the alkyl substituents were added with the HADD utility of SHELXTL/PC (Sheldrick, 1990). The two H atoms attached to C30 appear as four H atoms with equal site occupancies; the three terminal H atoms attached to C31A/C31B were included in six positions. Other H atoms were identified from the Fourier map and were refined isotropically.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC. Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXL93. Geometric calculations: PARST (Nardelli, 1983).

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Bis(thiourea)cadmium Halides

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Abstract

The crystals of dichlorobis(thiourea-S)cadmium, $[\text{CdCl}_2\{\text{SC}(\text{NH}_2)_2\}_2]$, (I), and dibromobis(thiourea-S)cadmium, $[\text{CdBr}_2\{\text{SC}(\text{NH}_2)_2\}_2]$, (II), are orthorhombic ($Pmn2_1$ and $Pnam$, respectively), while those of diiodobis(thiourea-S)cadmium, $[\text{CdI}_2\{\text{SC}(\text{NH}_2)_2\}_2]$, (III), are monoclinic ($P2_1/c$). In all these compounds, two S atoms from two thiourea molecules and two X ($X = \text{halogen}$) atoms coordinate to Cd in tetrahedral arrangements. Crystal packing is mainly determined by N—H...X hydrogen bonds, but is different in all three cases. The average Cd—X distance increases from 2.541 (1) Å in (I) to 2.655 (3) Å in (II) and 2.782 (1) Å in (III), whereas the average Cd—S distances in the three compounds are quite similar, their values being 2.517 (1), 2.522 (2) and 2.526 (2) Å, for (I), (II) and (III), respectively.

Comment

Thiourea is a chemically interesting ligand that has been widely studied [there are more than 700 structures of