TEXSAN (Molecular Structure Corporation/Rigaku Corporation, 1998). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1053). Services for accessing these data are described at the back of the journal.

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Dichloro[2,2′-(2,5-dithiahexamethylene)dipyridine-*N*,*N*′,*S*,*S*′]nickel(II)

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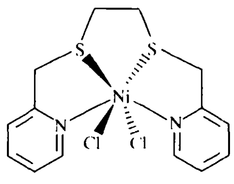
Abstract

The title complex, *cis*-$[NiCl_2(C_{14}H_{16}N_2S_2)]$, has twofold crystallographic symmetry and the Ni atom has an octahedral coordination with two *cis* thioether S atoms, two *trans* pyridyl N atoms and two *cis* chloride ions. The main dimensions are Ni—N 2.1078 (16), Ni—S 2.4316 (7) and Ni—Cl 2.3855 (6) Å.

Comment

The identification of nickel complexes capable of generating methane from methyl-coenzyme M has proved to be difficult (Jaun & Pfaltz, 1988) and we recently reported an Ni^{II} compound which has coordinating tendencies towards the coenzyme (Pandiyan *et al.*, 1997*a*). Synthetic model studies of metalloenzymes have been used to illustrate the structural involvement on the biological functions (Stolzenberg & Zhang, 1997; Stolzenberg & Stershic, 1987; Murali *et al.*, 1994; Nishida & Takahashi, 1988; Pandiyan *et al.*, 1992, 1995, 1996, 1997*a*,*b*; Palaniandavar *et al.*, 1995; Drain *et al.*, 1988). The ligand 2,2′-(2,5-dithiahexamethylene)dipyridine (*L*) was synthesized and the spectroscopic biological studies on these complexes are under process in our laboratory.

In the structure of the title compound, (I), the Ni atom lies on a twofold axis of the *Pbcn* space group, while the remaining atoms are in general positions (Fig. 1). The metal center is coordinated by two thioether S atoms, two pyridyl N atoms and two chloride ions. The coordination bond distances and the bond angles are presented in Table 1. The greatest deviation from an idealized octahedral geometry, 12.21 (9)°, is observed for the pyridyl N atoms with Ni1. Atoms S1, $S1^i$, N1 and $N1^i$ are almost coplanar, with a calculated maximum deviation of 0.052 Å for S1 and $S1^i$ [symmetry code (i): $1-x, y, \frac{1}{2}-z$]. We can then consider the coordination environment as distorted octahedral with the apical positions occupied by the N atoms. The bite angle N1—Ni1—S1 [81.78 (5)°] is due to the steric hindrance of the five-membered ring formed by Ni1, N1, C3, C2 and S1. On the other hand, the deviation from an idealized geometry [6.00 (3)°] observed for the angle Cl1—Ni1—$Cl1^i$ is rather due to the electronic repulsion of the Cl atoms in a *cis* configuration. Despite a different point



(I)

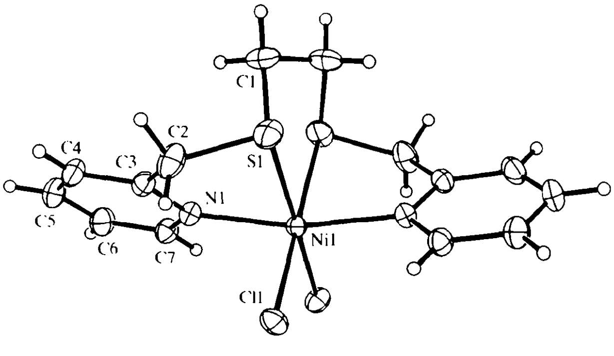


Fig. 1. The structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

group (*mmm* instead of $\bar{1}$), compound (I) displays a similar geometry to that reported for a cation containing the same ligand, $[\mathrm{Ni^{II}}L(\mathrm{CH_3CN})_2]^{2+}$ (Adhikary *et al.*, 1993).

The crystal packing of (I) is stabilized by a virtually linear network of weak hydrogen bonds, involving the Cl atoms and one H atom bonded to C1, with a separation of 2.74 Å (Table 2). This network forms molecular chains running along the *b* axis of the cell.

Experimental

$\mathrm{NiCl_2{\cdot}6H_2O}$ and 1,2-ethylenedithiol were used as received from Aldrich. The ligand 2,2′-(2,5-dithiahexamethylene)dipyridine (*L*) was synthesized as reported (Adhikary *et al.*, 1993). The nickel complex was formed when the ligand (1 mmol) dissolved in methanol (10 ml) was added to a solution of $\mathrm{NiCl_2{\cdot}6H_2O}$ (1 mmol) in methanol (10 ml). The green compound obtained was collected, washed with a small amount of methanol and dried over $\mathrm{P_4O_{10}}$. A solution of the nickel(II) complex (0.01 g) dissolved in methanol (10 ml) was allowed to evaporate. The fine green single crystals obtained were suitable for X-ray diffraction analysis.

Crystal data

$[\mathrm{NiCl_2(C_{14}H_{16}N_2S_2)}]$
$M_r = 406.02$
Orthorhombic
Pbcn
$a = 14.5297\,(16)$ Å
$b = 8.2314\,(14)$ Å
$c = 14.3684\,(18)$ Å
$V = 1718.5\,(4)$ Å^3
$Z = 4$
$D_x = 1.569$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 4.87–12.49°$
$\mu = 1.676$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.6 × 0.3 × 0.3 mm
Green

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (Fait, 1991)
$T_{\min} = 0.251$, $T_{\max} = 0.278$
2702 measured reflections
2066 independent reflections
1616 reflections with $I > 2\sigma(I)$

$R_{\mathrm{int}} = 0.018$
$\theta_{\max} = 27.99°$
$h = -1 \rightarrow 19$
$k = -1 \rightarrow 10$
$l = -1 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: 6.85%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.069$
$S = 1.013$
2066 reflections
97 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0206P)^2 + 1.0130P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.245$ e Å^{-3}
$\Delta\rho_{\min} = -0.322$ e Å^{-3}
Extinction correction: *SHELX*97
Extinction coefficient: 0.0053 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni1—N1	2.1078 (16)	S1—C2	1.801 (3)
Ni1—Cl1	2.3855 (6)	S1—C1	1.821 (3)
Ni1—S1	2.4316 (7)		
N1—Ni1—N1$^{\mathrm{i}}$	167.79 (9)	N1—Ni1—S1	81.78 (5)
N1—Ni1—Cl1	92.51 (5)	Cl1—Ni1—S1	88.58 (2)
N1—Ni1—Cl1$^{\mathrm{i}}$	95.65 (5)	S1$^{\mathrm{i}}$—Ni1—S1	86.94 (4)
Cl1—Ni1—Cl1$^{\mathrm{i}}$	96.00 (3)	C2—S1—C1	102.10 (13)
N1—Ni1—S1$^{\mathrm{i}}$	89.35 (5)	C2—S1—Ni1	93.41 (8)
Cl1—Ni1—S1$^{\mathrm{i}}$	174.85 (2)	C1—S1—Ni1	99.72 (10)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···Cl1$^{\mathrm{i}}$	0.97	2.74	3.676 (3)	163

Symmetry code: (i) $x, 1 + y, z$.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELX*97. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995). Software used to prepare material for publication: *SHELX*97.

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trans-Diiodobis(triphenylphosphine)-palladium(II)

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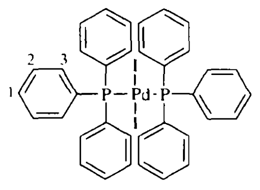
Abstract

The title compound, [$PdI_2\{P(C_6H_5)_3\}_2$], has the Pd atom located on a crystallographic inversion centre and has a *trans*-square-planar configuration. The Pd—I and Pd—P distances are 2.5975 (3) and 2.3504 (10) Å, respectively. This is the first reported structure of the title compound in an unsolvated form.

Comment

In the course of our studies on the synthesis of novel platinum compounds, we sought to make some new pyridine-type ligands. Our route to these compounds follows the published procedure of using a Grignard reagent with a dihalopyridine, catalyzed by tetrakis(triphenylphosphine)palladium (Minato *et al.*, 1980). The title compound, (I), was isolated as orange crystals from amongst the white crystals of the desired product. It was of interest to investigate the crystal structure of this compound in view of earlier discussions of the red chloroform solvate (Kubota *et al.*, 1991) and the yellow dichloromethane solvate (Debaerdemaeker *et al.*, 1973) in relation to solvation, intermolecular Pd···I interactions and intramolecular Pd···H interactions.



(I)

The molecular structure of the title compound is illustrated in Fig. 1. The Pd atom is located on a crystallographic inversion centre which implies a *trans* geometry with two exactly equal Pd—I distances and two equal Pd—P distances; also, this square-planar complex has the Pd and four ligand donor atoms accurately in a single plane. The Pd—I and Pd—P bond distances are in excellent agreement with those reported previously for the solvates (Table 2). The present structure is devoid of solvent and furthermore does not contain any solvent-accessible spaces (*PLATON*; Spek, 1998).

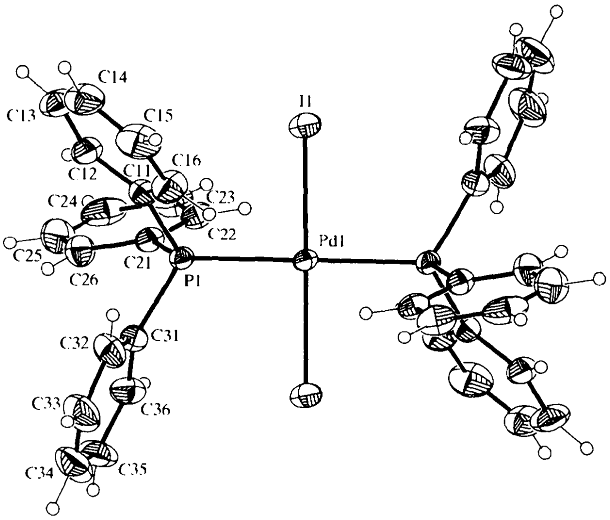


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

In the yellow dichloromethane solvate (Debaerdemaeker *et al.*, 1973), a Pd···H separation of 3.18 Å was observed, and this was taken as evidence of octahedral coordination with weak Pd···H interactions. Whilst this distance is greater than the sum of the van der Waals radii of Pd and H, the authors pointed out that since the hydrogen was placed at a calculated position, this bond length is artificial. The real evidence for the Pd···H interaction, they maintain, is the distortion that such an interaction would induce in the phenyl ring; this distortion is observed, with one bond length stretched to 1.491 Å, one reduced to 1.294 Å and the angles deviating substantially from 120°.

The red chloroform solvate (Kubota *et al.*, 1991) is reported to have no intermolecular Pd···I or intramolecular Pd···H interactions, which the authors note is in contrast to the related red complex *trans*-[$PdI_2(PPhMe_2)$] (Bailey & Mason, 1968), which does have intermolecular Pd···I interactions. The title complex, with no intermolecular Pd···I or intramolecular Pd···H interactions, but also no solvation, is orange. This would suggest that the colour is more a function of solvation rather than intermolecular interactions.

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