Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1026). Services for accessing these data are described at the back of the journal.

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Bis[bis(ethylenediamine-N,N')($\mu_{N,S}$-thiocyanato)nickel(II)] Bis(hexafluorophosphate)

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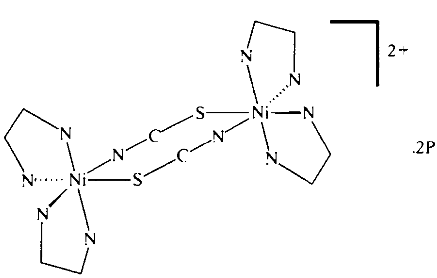
Abstract

The title compound, $[Ni_2(NCS)_2(C_2H_8N_2)_4](PF_6)_2$ or $[Ni(en)_2(\mu_{N,S}\text{-}NCS)]_2[PF_6]_2$ (en = ethylenediamine), has been synthesized *via* a molecular rearrangement reaction of *trans*-$Ni(en)_2(NCS)_2$. It consists of dibridged $[Ni(en)_2(\mu_{N,S}\text{-}NCS)]_2$ cations with the NCS ligands forming a *cis* arrangement at the nickel centres. A three-dimensional intermolecular hydrogen-bonding network is observed between the amine protons of the en ligands and the F atoms of the PF_6^- anions.

Comment

The cationic component of the title compound, (1), consists of a pair of pseudo-octahedrally coordinated Ni atoms, linked by two bridging thiocyanato ligands to give a dimeric species. The symmetry of (1) is such as to place a crystallographic inversion centre at the centre of the dimer. Hexafluorophosphate groups form the anionic component of this complex salt, with each PF_6^- group sitting on a crystallographic twofold axis. The arrangement of these ions in the asymmetric unit of (1) is shown in Fig. 1. As may be noted from this figure, the two thiocyanate bridges of (1) show only slight deviations from coplanarity. The dihedral angle formed by the planes containing atoms Ni1, S1, C1 and Ni1, S1, N1 is 3.5 (1)°.



(1)

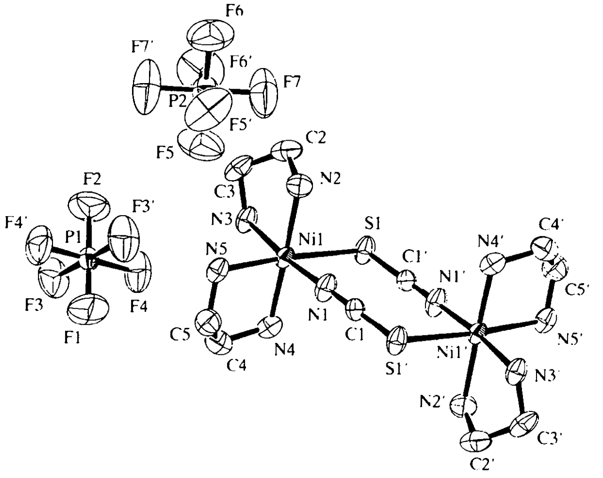


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of $[Ni(en)_2(\mu_{N,S}\text{-}NCS)]_2[PF_6]_2$, (1). All atoms are represented by 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The analogous iodide and perchlorate salts of (1) have previously been communicated (Svelasvili, 1966); however, this is the first report of a salt containing the PF_6^- counter-ion. Other related dithiocyanato-bridged species have been observed, notably for $[Ni(tren)_2(\mu_{N,S}\text{-}NCS)]_2[BPh_4]_2$ (tren = 2,2′,2″-triaminotriethylamine; Duggan & Hendrickson, 1974),

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$[Ni(benzylamine)_3(NCS)(\mu_{N,S}\text{-}NCS)]_2$ (Taniguchi & Ouchi, 1986) and $[Ni(terpy)(NCS)(\mu_{N,S}\text{-}NCS)]_2$ (terpy = 2,2′:6′,2″-terpyridine; Rojo *et al.*, 1991). Recently, a one-dimensional polymeric polymorph of (1), [*catena*-$(\mu_{N,S}\text{-}NCS)\{Ni(en)_2\}]PF_6$, has been reported (Monfort *et al.*, 1994). As in the case of (1), neighbouring nickel(II) ions are linked by thiocyanato bridging ligands in a *cis* geometry; however, in this case, alternate bridges are formed at approximately 90° to one another. Thus, a cationic helical chain is formed whose axis is parallel to the crystallographic *c* axis.

A significant *trans* effect is noted at the Ni centres, with average Ni—N(en) bond distances of 2.083 (2) and 2.114 (2) Å, *cis* and *trans* to the bridging thiocyanato groups, respectively. In contrast to the findings of Svelasvili (1966) for $[Ni(en)_2(\mu_{N,S}\text{-}NCS)]_2I_2$, the *trans* effect observed in (1) does not extend to C—N bond asymmetry in the ethylenediamine rings.

The significant puckering of the chelating en rings of (1) can be quantified by the dihedral angle (ω) between the planes defined, for example, by N2—C2—C3 and C2—C3—N3. The values of ω of 55.3 (1) and 53.1 (1)° for the N2–N3 and N4–N5 en rings are typical of that found in other bis-chelating en complexes (Cramer *et al.*, 1976).

A three-dimensional intermolecular hydrogen-bonding network is observed in (1) between the amine protons of the en ligands and the fluorine Lewis base (acceptor) sites on the PF_6 groups (Table 3). Strong hydrogen bonds in (1) occur between amine protons that are both parallel and oblique to the pseudo-C_3 axis of the Ni centre. Weaker intermolecular hydrogen bonds are also observed between amine protons and Lewis base sites at S atoms of the thiocyanate groups (Table 3). Relatively weak intramolecular hydrogen bonding also occurs in (1) between amine protons and nitrogen acceptor sites on adjacent chelate rings.

Intermolecular hydrogen bonding is a feature commonly observed in many compounds containing chelating en rings. In the case of bis-chelating molecules, strong intermolecular bonds have been observed not only between amine protons and counter-anions such as PF_6^- (James *et al.*, 1998) and ClO_4^- (Meyer *et al.*, 1982), but also between amine and aqua ligand protons to non-coordinated BF_4^- anions (Tomlinson *et al.*, 1976).

Experimental

The precursor *trans*-$Ni(en)_2(NCS)_2$ was prepared from $Ni(NCS)_2.0.5H_2O$ and ethylenediamine in the manner reported elsewhere (Brown & Lingafelter, 1963). The stereochemistry of this compound was confirmed as *trans* by single-crystal X-ray diffraction. To an aqueous solution of *trans*-$Ni(en)_2(NCS)_2$ (1 mmol, 30 ml) and NH_4PF_6 (2 mmol) was added a methanolic solution of pyrazine (1 mmol, 10 ml) with rapid stirring. No immediate precipitate resulted. Upon reducing the volume to about 20 ml on a hotplate and allowing the solution to stand in air for 3 weeks, purple crystals of $[Ni(en)_2(\mu_{N,S}\text{-}NCS)]_2[PF_6]_2$, (1), were formed along with pale purple crystals of $[Ni(en)_2(NCS)_2]_2[Ni(en)_3][PF_6]_2$, (2). The structural characterization of (2) is discussed elsewhere (James *et al.*, 1998).

Crystal data

$[Ni_2(NCS)_2(C_2H_8N_2)_4](PF_6)_2$
$M_r = 763.87$
Monoclinic
$C2/c$
$a = 15.865\ (3)$ Å
$b = 16.781\ (3)$ Å
$c = 12.691\ (3)$ Å
$\beta = 124.72\ (2)°$
$V = 2777\ (1)$ Å^3
$Z = 4$
$D_x = 1.827$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10.0\text{–}15.0°$
$\mu = 1.73$ mm^{-1}
$T = 273.2$ K
Plate
0.350 × 0.155 × 0.125 mm
Purple

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$\omega\text{–}2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.74$, $T_{max} = 0.80$
3981 measured reflections
3483 independent reflections

2615 reflections with $I > 2.5\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.47°$
$h = -20 \rightarrow 17$
$k = -1 \rightarrow 21$
$l = -1 \rightarrow 16$
3 standard reflections every 50 reflections intensity decay: 2.4%

Refinement

Refinement on F
$R = 0.034$
$wR = 0.047$
$S = 1.49$
2615 reflections
238 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o) + 0.0003|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni1	0.80354 (2)	0.17584 (2)	0.23253 (3)	0.03089 (7)
S1	0.86936 (5)	0.12724 (4)	0.09688 (6)	0.0423 (2)
P1	1	0.13401 (6)	3/4	0.0400 (2)
P2	1/2	0.00078 (8)	1/4	0.0541 (3)
F1	1	0.2263 (2)	3/4	0.135 (2)
F2	1	0.0412 (2)	3/4	0.110 (1)
F3	1.1098 (2)	0.1333 (2)	0.8799 (2)	0.1019 (9)
F4	1.0477 (2)	0.1339 (2)	0.6703 (2)	0.0922 (8)
F5	0.5856 (2)	0.0659 (2)	0.3016 (3)	0.121 (1)
F6	0.4144 (2)	−0.0651 (2)	0.1956 (3)	0.128 (1)
F7	0.4928 (2)	0.0004 (3)	0.1224 (3)	0.135 (1)
N1	0.7100 (2)	0.2592 (1)	0.0965 (2)	0.0461 (6)
N2	0.6910 (2)	0.0883 (2)	0.1453 (2)	0.0456 (6)
N3	0.8913 (2)	0.0823 (1)	0.3605 (2)	0.0405 (5)
N4	0.9201 (2)	0.2608 (1)	0.3243 (2)	0.0426 (6)
N5	0.7662 (2)	0.2222 (2)	0.3561 (2)	0.0418 (6)
C1	0.6779 (2)	0.3063 (1)	0.0168 (2)	0.0305 (5)

C2	0.7386 (3)	0.0100 (2)	0.1980 (4)	0.0564 (8)
C3	0.8178 (2)	0.0189 (2)	0.3396 (3)	0.0550 (8)
C4	0.9242 (3)	0.2936 (2)	0.4346 (3)	0.0550 (8)
C5	0.8170 (3)	0.2995 (2)	0.4017 (3)	0.0539 (8)

Table 2. *Selected geometric parameters (Å, °)*

Ni1—S1	2.6014 (8)	N1—C1	1.148 (3)
Ni1—N1	2.055 (2)	N2—C2	1.473 (4)
Ni1—N2	2.078 (2)	N3—C3	1.486 (4)
Ni1—N3	2.113 (2)	N4—C4	1.471 (4)
Ni1—N4	2.087 (2)	N5—C5	1.462 (4)
Ni1—N5	2.115 (2)	C2—C3	1.503 (5)
S1—C1^{i}	1.630 (2)	C4—C5	1.506 (5)
S1—Ni1—N1	91.56 (7)	N3—Ni1—N5	92.5 (1)
S1—Ni1—N2	88.44 (8)	N4—Ni1—N5	82.4 (1)
S1—Ni1—N3	86.50 (7)	Ni1—S1—C1^{i}	102.43 (9)
S1—Ni1—N4	91.23 (7)	Ni1—N1—C1	162.5 (2)
S1—Ni1—N5	173.47 (7)	Ni1—N2—C2	109.0 (2)
N1—Ni1—N2	92.5 (1)	Ni1—N3—C3	106.7 (2)
N1—Ni1—N3	174.9 (1)	Ni1—N4—C4	109.4 (2)
N1—Ni1—N4	89.4 (1)	Ni1—N5—C5	107.2 (2)
N1—Ni1—N5	89.97 (9)	S1^{i}—C1—N1	179.1 (2)
N2—Ni1—N3	82.8 (1)	N2—C2—C3	108.5 (3)
N2—Ni1—N4	178.06 (9)	N3—C3—C2	108.7 (3)
N2—Ni1—N5	97.8 (1)	N4—C4—C5	109.3 (3)
N3—Ni1—N4	95.29 (9)	N5—C5—C4	109.4 (3)

Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, -z$.

Table 3. *Hydrogen-bonding distances (Å)*

D—H···*A*	H···*A*	*D*—H···*A*	H···*A*
N2—H7···F5	2.45 (4)	N3—H2···F3^{iii}	2.81 (4)
N2—H7···F7	2.65 (3)	N3—H2···F4	2.58 (3)
N2—H8···F6^{i}	2.79 (4)	N4—H10···F6^{iv}	2.52 (3)
N2—H8···F7^{i}	2.62 (3)	N5—H15···F1^{v}	2.93 (3)
N3—H1···F2^{ii}	2.70 (3)	N5—H16···F3^{iii}	2.32 (3)
H···*A*	H···*A*	H···*A*	H···*A*
H1···S1^{vi}	2.97 (3)	H9···S1^{vi}	2.83 (3)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $x, -y, z+\frac{1}{2}$; (iii) $2-x, y, \frac{3}{2}-z$; (iv) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (v) $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$; (vi) $2-x, y, \frac{1}{2}-z$.

The structure was solved by direct methods and developed by alternating cycles of difference Fourier syntheses and full-matrix least-squares refinements. The positions of the atoms were determined unequivocally. The non-H atoms were refined anisotropically, while the H atoms were refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). 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: BK1401). Services for accessing these data are described at the back of the journal.

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Bis(dimethylammonium) Hexachlorotellurate(IV)

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Abstract

The title compound, $[(CH_3)_2NH_2]_2[TeCl_6]$, is isostructural with $[(CH_3)_2NH_2]_2[SnCl_6]$ and the high-density form of $[(CH_3)_2NH_2]_2[PtCl_6]$. It consists of a slightly distorted $[TeCl_6]^{2-}$ octahedron and $[(CH_3)_2NH_2]^+$ ions connected by a weak bifurcated hydrogen bond.

Comment

$[(CH_3)_2NH_2]_2[TeCl_6]$, (I), was reported to be isomorphous with $[(CH_3)_2NH_2]_2[SnCl_6]$ (Ben Ghozlen & Daoud, 1981; Knop *et al.*, 1983) from X-ray powder diffraction data taken at room temperature (Ishida *et al.*, 1984). The phase transitions and the molecular motions of the cation and anion were studied by ^{1}H NMR (Ishida *et al.*, 1984), ^{35}Cl NQR (Horiuchi *et al.*, 1985; Ishikawa *et al.*, 1989) and ^{2}H NMR (Ikeda *et al.*, 1989) under the assumption that the Te salt has the same atomic arrangement as the Sn salt. The 180° flip motion of the cation about its pseudo-C_2 axis and the 90° re-orientational jumps of the anion around the Te—Cl bond axis were found to occur at room temperature in the Te salt with smaller activation energies than those determined in the Sn salt. This implies that the ions in the Te salt are bound more loosely than in the Sn salt.