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Bis[bis(2-aminoethyl-*N*)sulfide-*S*]nickel(II) Bis(hexafluorophosphate)

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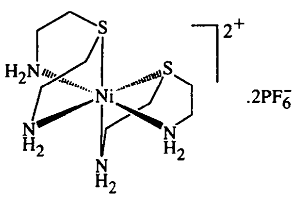
Abstract

The structure of the title complex, $[Ni(C_4H_{12}N_2S)_2](PF_6)_2$, shows a distorted octahedral geometry around the nickel centre, with the two S atoms mutually *cis*.

Comment

The bis(2-aminoethyl)sulfide ligand, (2), is an important starting material in the synthesis of the mixed N/S-donor macrocycle 4,7-diaza-1-thiacyclononane (Hart, Boeyens, Michael & Hancock, 1983). The structure determination of its nickel complex, (1), shows a 1:2 metal–ligand stoichiometry, with the metal coordinated by four N and two S atoms in a distorted octahedral geometry. The Ni—N distances lie in the range 2.102 (5)–2.141 (5) Å and the Ni—S distances are 2.462 (2) and 2.467 (3) Å. The two S atoms are mutually *cis* [S4—Ni—S41 96.04 (8)°], an arrangement which has also been shown for the analogous perchlorate salt (Hart, Boeyens & Hancock, 1983), as well as for the $[Co^{III}(2)Cl_3]$ complex (Hammershfi, Larsen & Larsen, 1978).



(1)

The observed orientation of the ligands, which are rotated by *ca* 60° from the eclipsed conformation, results in a separation of 3.664 (4) Å between the S4 and S41 atoms (the sum of their van der Waals radii is 3.70 Å). In contrast, the Cu^{II} complex of (2) shows the four N atoms in the equatorial plane with the two S atoms occupying the axial sites (Boeyens, Dobson & Hancock, 1985). The coordination sphere in (1) is similar to that in the analogous perchlorate salt, which has bond lengths Ni—S 2.455 (5) and 2.463 (6), and Ni—N 2.05–2.17 (2) Å (Hart, Boeyens & Hancock, 1983).

One of the PF_6^- anions lies in a general position; the remaining charge balance is provided by one anion on an inversion centre and one on a twofold axis.

Intermolecular contacts in complex (1) are primarily N—H···F contacts of 2.29 Å or more, but there are also S···S^i [symmetry code: (i) $1-x$, $1-y$, $-z$] contacts between S4 atoms in cations related by centres of inversion; at distances of 3.654 (4) Å, these interactions fall just within the sum of the corresponding van der Waals radii (3.70 Å).

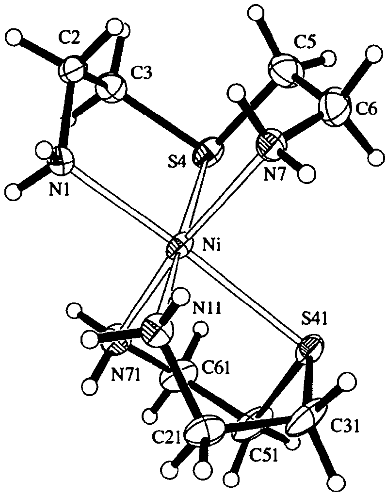


Fig. 1. A view of the cation in (1) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii.

Experimental

Bis(2-aminoethyl)sulfide was synthesized according to a known route (Lavery, 1983). An ethanolic solution of the ligand was added to an ethanolic solution of $Ni(NO_3)_2.3H_2O$. The solution instantly turned purple and was refluxed for 1 h to ensure complete reaction. The solvent was removed *in vacuo* and the residue redissolved in water. To this solution was added an excess of ammonium hexafluorophosphate and the resulting precipitate was collected by filtration and recrystallized from acetonitrile and diethyl ether. Elemental analysis: found C 16.5, H 4.5, N 9.3%, $C_8H_{24}F_{12}N_4NiP_2S_2$ requires C 16.3, H 4.1, N 9.5%. Crystals of diffraction quality were grown by slow diffusion of diethyl ether into a solution of the complex in acetonitrile.

Crystal data

$[Ni(C_4H_{12}N_2S)_2](PF_6)_2$
M_r = 589.08

Mo $K\alpha$ radiation
λ = 0.71073 Å

Monoclinic
$I2/a$
a = 17.582 (12) Å
b = 9.451 (8) Å
c = 24.558 (17) Å
β = 98.88 (8)°
V = 4032 (5) Å^3
Z = 8
D_x = 1.941 Mg m^{-3}
D_m not measured

Cell parameters from 32 reflections
θ = 26–30°
μ = 1.440 mm^{-1}
T = 150.0 (2) K
Columnar
0.70 × 0.50 × 0.20 mm
Purple

Data collection

Stoe Stadi-4 four-circle diffractometer with an Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986)
ω–2θ scans
Absorption correction: calculated from ΔF (Walker & Stuart, 1983)
$T_{\min}$ = 0.52, $T_{\max}$ = 0.75
8991 measured reflections

3514 independent reflections
2840 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.0455
$\theta_{\max}$ = 25.05°
$h = -15 \rightarrow 20$
$k = -11 \rightarrow 10$
$l = -29 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0647
$wR(F^2)$ = 0.3020
S = 1.044
3501 reflections
265 parameters
H atoms introduced at calculated positions
$w = 1/[\sigma^2(F_o^2) + (0.231P)^2 + 13.02P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.003$
$\Delta\rho_{\max}$ = 1.47 e Å^{-3} (0.96 Å from Ni)
$\Delta\rho_{\min}$ = −1.81 e Å^{-3} (1.03 Å from Ni)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for nis3n2*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Ni	0.58827 (4)	0.24704 (7)	−0.12065 (3)	0.0154 (4)
N1	0.4715 (3)	0.2248 (6)	−0.1563 (2)	0.0189 (12)
C2	0.4176 (4)	0.2397 (7)	−0.1157 (3)	0.0209 (14)
C3	0.4366 (4)	0.3730 (7)	−0.0810 (3)	0.0218 (14)
S4	0.53614 (9)	0.3807 (2)	−0.04866 (7)	0.0216 (5)
C5	0.5366 (5)	0.2377 (8)	0.0023 (3)	0.030 (2)
C6	0.5932 (4)	0.1234 (8)	−0.0069 (3)	0.030 (2)
N7	0.5841 (3)	0.0763 (6)	−0.0639 (2)	0.0201 (12)
N11	0.6314 (3)	0.1186 (5)	−0.1788 (2)	0.0192 (11)
C21	0.7127 (4)	0.1482 (7)	−0.1840 (3)	0.0231 (14)
C31	0.7603 (4)	0.1527 (8)	−0.1280 (3)	0.030 (2)
S41	0.72506 (9)	0.2832 (2)	−0.08248 (7)	0.0214 (5)
C51	0.7385 (4)	0.4504 (7)	−0.1165 (4)	0.031 (2)
C61	0.6626 (4)	0.5290 (7)	−0.1301 (3)	0.0263 (15)
N71	0.6040 (3)	0.4384 (6)	−0.1630 (2)	0.0223 (12)
P1	1.02317 (9)	−0.2005 (2)	0.17829 (7)	0.0218 (5)
F11	1.1097 (3)	−0.2160 (5)	0.2088 (2)	0.0401 (12)
F12	0.9368 (2)	−0.1786 (5)	0.1486 (2)	0.0382 (11)
F13	0.9941 (3)	−0.3046 (5)	0.2227 (2)	0.0401 (12)
F14	1.0523 (2)	−0.0957 (5)	0.1343 (2)	0.0358 (11)
F15	1.0329 (4)	−0.3314 (5)	0.1397 (2)	0.056 (2)
F16	1.0120 (3)	−0.0678 (5)	0.2168 (2)	0.0439 (12)
P2	1/4	1/4	1/4	0.0263 (7)
F21	0.3198 (3)	0.3605 (5)	0.2536 (2)	0.0389 (11)
F22	0.2677 (3)	0.1955 (5)	0.1914 (2)	0.0363 (11)
F23	0.1928 (3)	0.3673 (5)	0.2196 (2)	0.0408 (11)
P3	3/4	0.7967 (3)	0.0000	0.0233 (6)
F31	3/4	0.6278 (6)	0.0000	0.044 (2)
F32	3/4	0.9682 (6)	0.0000	0.041 (2)
F33	0.7470 (4)	0.7962 (6)	0.0640 (2)	0.060 (2)
F34	0.8414 (3)	0.7965 (6)	0.0133 (3)	0.058 (2)

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

Ni—N1	2.115 (6)	S4—C5	1.841 (8)
Ni—S4	2.462 (2)	C5—C6	1.509 (10)
Ni—N7	2.141 (5)	C6—N7	1.455 (9)
Ni—N11	2.102 (5)	N11—C21	1.482 (8)
Ni—S41	2.467 (3)	C21—C31	1.495 (10)
Ni—N71	2.126 (5)	C31—S41	1.836 (8)
N1—C2	1.482 (9)	S41—C51	1.820 (7)
C2—C3	1.529 (9)	C51—C61	1.518 (9)
C3—S4	1.809 (7)	C61—N71	1.480 (9)
N1—Ni—S4	84.4 (2)	S4—Ni—N71	90.3 (2)
N1—Ni—N7	93.8 (2)	N7—Ni—N11	93.4 (2)
N1—Ni—N11	95.2 (2)	N7—Ni—S41	89.2 (2)
N1—Ni—S41	177.0 (2)	N7—Ni—N71	168.5 (2)
N1—Ni—N71	94.2 (2)	N11—Ni—S41	84.6 (2)
S4—Ni—N7	82.2 (2)	N11—Ni—N71	94.1 (2)
S4—Ni—N11	175.6 (2)	S41—Ni—N71	82.8 (2)
S4—Ni—S41	96.04 (8)		
N1—C2—C3—S4	−53.6 (7)	N11—C21—C31—S41	−56.7 (6)
C2—C3—S4—C5	−69.7 (5)	C21—C31—S41—C51	−64.3 (5)
C3—S4—C5—C6	120.0 (6)	C31—S41—C51—C61	122.1 (6)
S4—C5—C6—N7	−49.8 (8)	S41—C51—C61—N71	−54.9 (7)

The non-standard space group (*I*2/*a*) was chosen to give a more orthogonal unit cell and thereby reduce correlation. The transformation matrix (101/010/$\bar{1}$00) yields the standard space group *C*2/*c* with cell constants a = 27.91 (2), b = 9.451 (8), c = 17.582 (12) Å and β = 119.61 (6)°.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: JZ1164). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraphenylphosphonium (Hydrogensulfido-*S*)trisulfidotungstate(VI)

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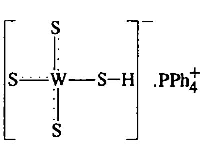
Abstract

The cations and anions of the title compound, $[(C_6H_5)_4P][W(HS)S_3]$, are separated by normal van der Waals distances. The ions each lie on $\bar{4}$ sites such that the H atom of the anion is disordered over four sites with 0.25 occupancies. The W—S distances in the anion are 2.171 (2) Å, with S—W—S angles of 108.1 (1) and 112.4 (2)°. In the cation, identical P—C distances of 1.793 (6) Å are observed, with C—P—C angles of 106.3 (4) and 111.1 (2)°.

Comment

The recently reported synthesis of $[(C_6H_5)_4P][W(C_2H_5S)S_3]$ (Boorman, Wang & Parvez, 1995) allowed exploration of the use of this complex, and other alkylated analogs, as a synthon for heterometallic sulfido–thiolato clusters. In this context, $[(C_6H_5)_4P][W(C_2H_5S)S_3]$ was reacted with CuCl using MeCN as solvent and from this solution, red crystals were isolated. Based on a parallel study of this reaction using ^{1}H NMR, it was believed that the crystals were likely to be a W–S–Cu cluster and hence, an X-ray structure determination was undertaken. The product is shown here to be $[(C_6H_5)_4P][W(HS)S_3]$, (1), for which no single-crystal structure determination had been reported previously. A structure based on X-ray powder data has been published (Königer-Ahlhorn, Schulze & Müller, 1977).



$$\left[\begin{array}{c} S \\ \vdots \\ S\text{—}W\text{—}S\text{—}H \\ \vdots \\ S \end{array}\right]^{-} .PPh_4^+$$

(1)

The observed W—S distance [2.171 (2) Å] is the average of one W—S and three W═S bonds due to disorder of the H atom over four sites. It is comparable with the distances previously reported (Boorman, Wang & Parvez, 1995) for $[(C_6H_5)_4P][W(C_2H_5S)S_3]$; W═S(ave.) 2.154 (3), W—S 2.323 (3) and W—S(ave.) 2.196 (3) Å. Previously reported structures of tungsten containing terminal SH groups involve the anions

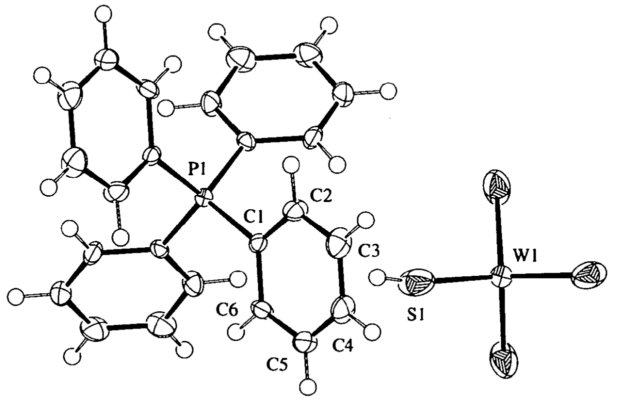


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound. Displacement ellipsoids are plotted at 50% probability level and H atoms have been assigned arbitrary radii; the disordered H atom of the anion has been plotted on one site only.

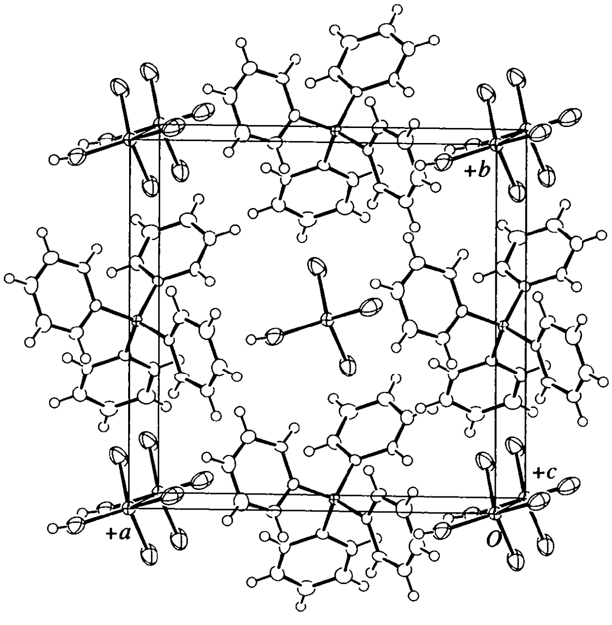


Fig. 2. Unit-cell packing of the title compound.