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1,4,10,13-Tetrathia-7,16-diazacyclooctadecanenickel(II) Nitrate Hydrate

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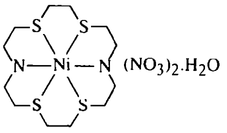
Abstract

The title compound, $[Ni(C_{12}H_{26}N_2S_4)](NO_3)_2.H_2O$, displays distorted octahedral coordination at the Ni atom with two almost planar S—N—S donor moieties normal to each other. The S atoms are in the equatorial plane, with the N atoms axial. The principal distances are Ni—S 2.403 (3)–2.445 (3) and Ni—N 2.069 (8)–2.118 (8) Å.

Comment

Macrocyclic crown ethers containing N and S atoms have been studied extensively in the fields of both chemistry and biology for their selective complexation with various metal cations (Pederson, 1967; Dunitz, Dobler, Seiler & Phizackerley, 1974; Ahrland, Chatt & Davis, 1958). What interested us most was their conformation and conformational change upon complexation with metal ions. In order to investigate the bonding and ligand behaviour in more detail, we synthesized the title compound, (I), and determined its crystal structure.



(I)

The macrocyclic ligand 1,4,10,13-tetrathia-7,16-diazacyclooctadecane (*L*) can coordinate as a hexadentate ligand with two possible octahedral configurations, *A* (in which the ligand is bent about each donor atom) and *B* (in which two S—N—S donor moieties are approximately planar), of its metal complexes (Black & Mclean, 1968, 1969). In both configurations, the four S atoms lie in the equatorial plane, with the two N donor atoms occupying the *trans* positions. From the *ORTEP* drawing (Johnson, 1965) of the title compound (Fig. 1), it can be seen that the the crown ether ring has the *B* configuration.

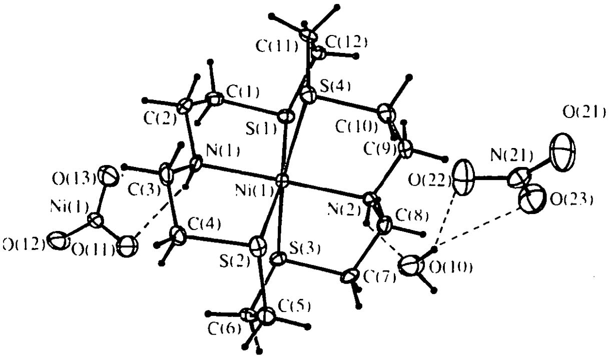


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids.

The coordination polyhedron around the Ni(1) atom is a distorted octahedron. The four equatorial N—S bond lengths (Table 2) are in the range 2.403 (3)–2.445 (3) Å, and are comparable with the lengths reported [2.370 (9)–2.435 (9) Å] for $[NiL]Cl_2.4H_2O$ (Wang, Miao & Zhou, 1991). The Ni—N distances in the title compound are 2.609 (8) and 2.118 (8) Å. The corresponding distances in $[NiL]Cl_2.4H_2O$ are 2.11 (2) and 2.14 (2) Å, while those in $[Ni(C_9H_{22}N_4)](ClO_4)_2$ are in the range 1.885–1.909 Å (Wei, Jin, Han, Xu & Ma, 1993). The remaining bond lengths and angles in the ligand are normal and close to those reported for $[PdL]Cl_2$ (Reid, Blake, Hyde & Schroder, 1988). The mean C—S, C—N and N—O bond lengths are 1.81, 1.46 and 1.20 Å, respectively. The N···N intracavity distance is 4.19 (1) Å and the *trans* S···S intracavity distances are 4.821 (4) and 4.824 (4) Å.

In an earlier paper, Dale (1980) defined the conformations of the crown rings (g^+ and g^- indicate *gauche* conformations with torsion angles of 0 to 120° and 0 to −120°, respectively, *a* indicates the antiperiplanar conformation with an angle of ±120 to 180° and $\underline{a}$ or $\underline{g}$ refers to the C—N conformation). Using these definitions, Ammon, Bhattacharjee, Shinkai & Honda (1984) first showed that four of the eight C—S bonds adopt an *anti* conformation in the thia-crown ring 2,2′-azobenzoyl-capped 1,4,10,13-tetrathia-7,16-diazacyclooctadecane. They then reported that all C—N bonds in the ligand *L* have *anti* conformations, with no *anti* conformations for C—S bonds (Ammon, Chandrasekhar & Bhattacharjee, 1984). We now find the conformations of the title compound to be ($g^-g^-\underline{a}$, $\underline{a}g^+a$, $g^+g^+g^+$, $ag^+\underline{a}$, $\underline{a}g^-g^-$, $g^+g^+g^+$) [from C(12)—S(1)—C(1)—C(2)], with two of the eight C—S bonds *anti*, six *gauche* and all C—N bonds *anti*.

Two NO_3^- ions are located beside the macrocyclic polyether ring and are connected to the ring and a water molecule by two intramolecular and two intermolecular hydrogen bonds (Table 3).

Experimental

The ligand was prepared according to the literature method of Black & Mclean (1969). 0.5 mmol of *L* and 0.5 mmol of anhydrous $[Ni(NO_3)_2]$ were each dissolved in 50 ml of ethanol.

The solution of L was slowly added to the $[Ni(NO_3)_2]$ solution under reflux, then most of the solvent was removed. After cooling to room temperature, the solution was filtered and the filtrate was allowed to evaporate at room temperature for several weeks, whereupon light-purple crystals of the title compound were obtained. The crystal density D_m was measured by pycnometry.

Crystal data

$[Ni(C_{12}H_{26}N_2S_4)](NO_3)_2.H_2O$
$M_r = 527.35$
Orthorhombic
$Pca2_1$
$a = 17.682\ (4)$ Å
$b = 10.292\ (3)$ Å
$c = 11.855\ (3)$ Å
$V = 2157.4$ Å^3
$Z = 4$
$D_x = 1.623$ Mg m^{-3}
$D_m = 1.630$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.68$–$11.87°$
$\mu = 1.314$ mm^{-1}
$T = 293$ K
Prism
$0.2 \times 0.2 \times 0.15$ mm
Purple

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.920$, $T_{\max} = 0.988$
2191 measured reflections
2000 independent reflections

1226 observed reflections $[F > 2.5\sigma(F)]$
$R_{\rm int} = 0.032$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 14$
3 standard reflections monitored every 400 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.034$
$wR = 0.037$
$S = 1.876$
1226 reflections
253 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0001F^2]$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.486$ e Å^{-3}
$\Delta\rho_{\min} = -0.150$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

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

	x	y	z	$U_{\rm eq}$
Ni(1)	0.40410 (5)	0.2103 (1)	0.000	0.0291 (3)
S(1)	0.3749 (1)	0.0320 (2)	0.1291 (2)	0.0403 (6)
S(2)	0.4075 (1)	0.3838 (3)	−0.1356 (2)	0.0475 (6)
S(3)	0.3675 (1)	0.3702 (2)	0.1411 (2)	0.0390 (6)
S(4)	0.4638 (1)	0.0488 (3)	−0.1180 (2)	0.0423 (6)
N(1)	0.2955 (4)	0.1801 (8)	−0.0592 (7)	0.038 (3)
N(2)	0.5140 (4)	0.2448 (7)	0.0642 (6)	0.035 (3)
O(11)	0.1735 (4)	0.3550 (8)	0.0272 (9)	0.085 (3)
O(12)	0.0564 (4)	0.3347 (8)	0.059 (1)	0.114 (4)
O(13)	0.1260 (5)	0.1758 (8)	0.0679 (1)	0.100 (4)
O(21)	0.8065 (5)	0.218 (1)	−0.242 (1)	0.114 (4)
O(22)	0.6892 (5)	0.263 (1)	−0.2430 (9)	0.108 (4)
O(23)	0.7528 (7)	0.280 (1)	−0.0973 (8)	0.109 (4)
O(10)	0.5981 (5)	0.4180 (8)	−0.0764 (8)	0.082 (3)
N(11)	0.1175 (4)	0.2882 (8)	0.0442 (8)	0.060 (3)
N(21)	0.7498 (6)	0.2555 (8)	−0.1953 (8)	0.062 (3)
C(1)	0.2820 (5)	−0.002 (1)	0.073 (1)	0.051 (3)
C(2)	0.2719 (5)	0.0441 (9)	−0.0468 (9)	0.048 (3)
C(3)	0.2886 (5)	0.227 (1)	−0.1764 (9)	0.060 (4)
C(4)	0.3113 (6)	0.366 (1)	−0.1858 (9)	0.051 (3)
C(5)	0.4003 (6)	0.525 (1)	−0.0464 (9)	0.054 (3)
C(6)	0.3496 (6)	0.5132 (9)	0.0556 (9)	0.048 (3)
C(7)	0.4608 (6)	0.404 (1)	0.1969 (9)	0.052 (3)
C(8)	0.5121 (6)	0.286 (1)	0.1804 (9)	0.053 (3)
C(9)	0.5654 (5)	0.137 (1)	0.0421 (9)	0.052 (3)
C(10)	0.5605 (5)	0.085 (1)	−0.0733 (9)	0.053 (3)
C(11)	0.4455 (6)	−0.1059 (9)	−0.0493 (9)	0.047 (3)
C(12)	0.4302 (5)	−0.1023 (9)	0.0757 (9)	0.044 (3)

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

Ni(1)—S(1)	2.445 (3)	Ni(1)—S(4)	2.416 (3)
Ni(1)—S(2)	2.403 (3)	Ni(1)—N(1)	2.069 (8)
Ni(1)—S(3)	2.433 (3)	Ni(1)—N(2)	2.118 (8)
S(1)—Ni(1)—S(2)	169.0 (1)	S(2)—Ni(1)—N(2)	95.3 (2)
S(1)—Ni(1)—S(3)	91.2 (1)	S(3)—Ni(1)—S(4)	168.4 (1)
S(1)—Ni(1)—S(4)	86.5 (1)	S(3)—Ni(1)—N(1)	95.0 (3)
S(1)—Ni(1)—N(1)	84.4 (3)	S(3)—Ni(1)—N(2)	83.3 (3)
S(1)—Ni(1)—N(2)	95.4 (3)	S(4)—Ni(1)—N(1)	96.1 (3)
S(2)—Ni(1)—S(3)	87.9 (1)	S(4)—Ni(1)—N(2)	85.5 (3)
S(2)—Ni(1)—S(4)	96.5 (1)	N(1)—Ni(1)—N(2)	178.4 (4)
S(2)—Ni(1)—N(1)	84.7 (3)		
C(12)—S(1)—C(1)—C(2)	−83.2 (8)		
C(1)—S(1)—C(12)—C(11)	69.5 (8)		
C(5)—S(2)—C(4)—C(3)	−134.1 (7)		
C(4)—S(2)—C(5)—C(6)	63.2 (9)		
C(7)—S(3)—C(6)—C(5)	67.0 (8)		
C(6)—S(3)—C(7)—C(8)	−131.2 (8)		
C(11)—S(4)—C(10)—C(9)	−79.0 (9)		
C(10)—S(4)—C(11)—C(12)	75.4 (8)		
C(3)—N(1)—C(2)—C(1)	178.1 (7)		
C(2)—N(1)—C(3)—C(4)	178.8 (8)		
C(9)—N(2)—C(8)—C(7)	176.8 (8)		
C(8)—N(2)—C(9)—C(10)	172.9 (8)		
S(1)—C(1)—C(2)—N(1)	−50.0 (9)		
N(1)—C(3)—C(4)—S(2)	57.6 (9)		
S(2)—C(5)—C(6)—S(3)	50.2 (10)		
S(3)—C(7)—C(8)—N(2)	54.3 (10)		
N(2)—C(9)—C(10)—S(4)	−49.9 (11)		
S(4)—C(11)—C(12)—S(1)	38.0 (10)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N(1)—H(1)···O(11)	0.88	2.20	2.99 (1)	149
N(2)—H(2)···O(10)	1.08	1.92	2.85 (1)	144
O(10)—H(O2)···O(22)	0.94	2.13	3.01 (1)	155
O(10)—H(O2)···O(23)	0.94	2.39	3.09 (1)	131
O(10)—H(O1)···O(11$^{\rm i}$)	0.87	2.17	2.96 (1)	150
O(10)—H(O1)···O(12$^{\rm i}$)	0.87	2.53	3.10 (1)	124

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

Structure solution and refinement used the *MolEN* package (Fair, 1990). Some H-atom coordinates were obtained from a difference map. The H-atom parameters were not refined but calculated.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1049). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[*R*-(*R**,*R**)]-(η^5-Cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine-*P*)]-(1-phenylphosphirane-*P*)iron(II) Hexafluorophosphate

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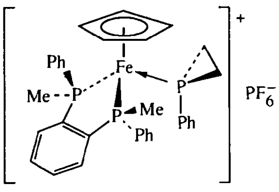
Abstract

The title compound, $[Fe(C_5H_5)(C_8H_9P)(C_{20}H_{20}P_2)]PF_6$, was obtained by spontaneous resolution of the racemate from acetone/diethyl ether solution. The cationic piano-stool iron(II) complex exhibits pseudo-octahedral coordination geometry, with Fe—P distances of 2.189 (3) and 2.178 (4) Å for the bidentate ligand, and 2.170 (3) Å for the phosphirane ligand. The bond parameters for the phosphirane ligand are in good agreement with those found for related complexes.

Comment

As part of our investigations of iron(II) complexes containing heterocyclic phosphorus and arsenic ligands, the compound (*R**,*R**)-(±)-[(η^5-C_5H_5){1,2-$C_6H_4(PMePh)_2$}Fe($PhPCH_2CH_2$)]PF_6, (*R**,*R**)-(1), was prepared by direct synthesis from 1-phenylphosphirane and (*R**,*R**)-(±)-[(η^5-C_5H_5){1,2-$C_6H_4(PMePh)_2$}-Fe(MeCN)]PF_6 (Bader, Kang, Pabel, Pathak, Willis & Wild, 1995). Orange (*R**,*R**)-(1) crystallized as a conglomerate of enantiomorphic crystals from acetone/diethyl ether solution. The crystal chosen for X-ray structure analysis was found to be the [*R*-(*R**,*R**)] enantiomer of the compound.



[*R*-(*R**,*R**)]-(1)

To our knowledge, this is the first cationic coordination complex of 1-phenylphosphirane to be characterized by X-ray crystallography. The molecular structure of the cation of [*R*-(*R**,*R**)]-(1) is depicted in Fig. 1. The complex has piano-stool geometry, with pseudo-octahedral coordination around the Fe atom. Bond distances and angles within the three-membered phosphirane ring (Table 2) differ little from the corresponding parameters for the neutral complexes [W(CO)$_5$($PhPCH_2CH_2$)] (Hung, Yang, Gray & Lammertsma, 1993) and *fac*-[Mo(CO)$_3$($PhPCH_2CH_2$)$_3$] (Kang, Pabel, Willis & Wild, 1994). Bond parameters for the [*R*-(*R**,*R**)]-[(η^5-C_5H_5){1,2-$C_6H_4(PMePh)_2$}Fe] fragment of the complex are also in good agreement with those found for related complexes (Hey, Willis

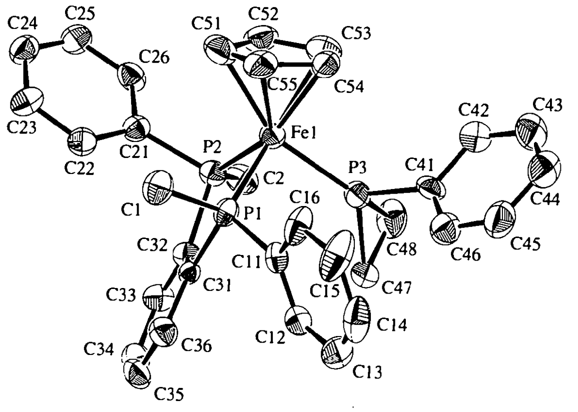


Fig. 1. An *ORTEP* plot (Johnson, 1965) of the cation of [*R*-(*R**,*R**)]-(1), with the non-H atoms shown as 30% probability ellipsoids and H atoms omitted for clarity.