[1-(3-Aminopropyl)-4,7-dithia-1-azacyclononane-κ^4N,N',S,S']bis(dimethylformamide-κO)nickel(II) bis(tetraphenylborate) acetonitrile disolvate

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In the title complex, [Ni(C₃H₇NO)₂(C₉H₂₀N₂S₂)](C₂₄H₂₀B)₂·2CH₃CN, the metal centre has a distorted octahedral environment, with four coordination sites occupied by two N- and two S-donor atoms from a 3-aminopropyl pendant arm derivative of the nine-membered macrocycle 1-aza-4,7-dithia-cyclononane, and the remaining two positions by two mutually *cis* dimethylformamide ligands.

Comment

The coordination chemistry of mixed thia–aza nine-membered macrocycles is of particular interest since the loss of threefold symmetry with respect to 1,4,7-triazacyclononane ([9]aneN₃) and the presence of both hard N- and soft S-donors can have interesting stereochemical consequences and thereby offer specific coordination selectivity (Danks *et al.*, 1998). Recently, we have reported on the coordination chemistry of nitrile and amino pendant arm derivatives of 1,4-diaza-7-thiacyclononane ([9]aneN₂S) and 1-aza-4,7-dithiacyclononane ([9]aneNS₂) with Pd^{II} and Cu^{II} (Arca *et al.*, 2003). A distorted square-pyramidal coordination is generally observed at these metal centres with 3-aminopropyl pendant arm derivatives of [9]aneN₂S and [9]aneNS₂ which show strong basal coordination of the N-donors of the macrocycle and of the primary amine group(s).

(I)
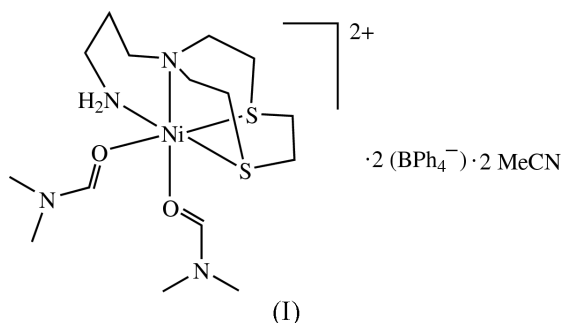
We report here the X-ray crystal structure of the title Ni^{II} complex, (I), obtained by reacting the 3-aminopropyl pendant arm derivative of [9]aneNS₂ with NiCl₂ in MeOH/H₂O followed by addition of excess sodium tetraphenylborate. Crystals were obtained by diffusion of Et₂O vapour first into a solution of acetonitrile and subsequently into a solution of the resulting solid in dimethylformamide. The metal centre is in a distorted octahedral geometry (Fig. 1) with two positions occupied by mutually *cis* dimethylformamide ligands and the remaining four by the two N- and two S-donor atoms of the pendant-arm macrocyclic ligand. The Ni—O and Ni—NH₂ bond lengths (Table 1) are both slightly shorter than the Ni—N4 distance which involves the tertiary macrocyclic N-donor.
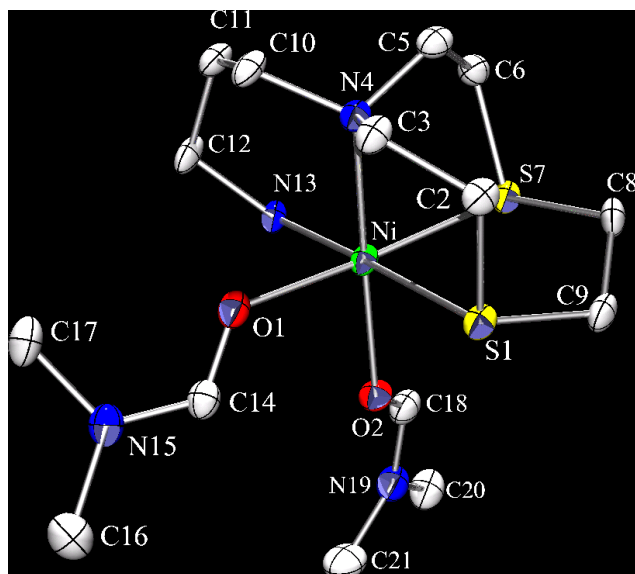
Figure 1
A view of the title cation, with displacement ellipsoids drawn at the 30% probability level. The two counter-anions and two solvent molecules are not shown, and H atoms have been omitted for clarity.

This leads to a trigonal elongation of the octahedron towards the triangular face formed by three of the macrocyclic donors. The S-donor *trans* to the NH₂ group lies slightly further from the metal than the one *trans* to the dimethylformamide donor O1.

Experimental

A solution of the ligand (30 mg, 0.136 mmol) and NiCl₂ (17.63 mg, 0.136 mmol) in MeOH/H₂O (10 ml, 1:1 v/v) was refluxed for 1 h. Excess sodium tetraphenylborate was added and a purple solid formed. Purple crystals were obtained as follows: first, Et₂O vapour was diffused into a solution of this solid in acetonitrile and a solid product isolated; second, this solid was dissolved in dimethylformamide and Et₂O vapour diffused into the solution (yield 51.7 mg, 33%). Found (calculated for C₆₇H₈₀B₂N₆NiO₂S₂): C 70.33 (70.23), H 6.98 (7.04), N 7.15% (7.33%).

Crystal data

Refinement

Table 1
Selected geometric parameters (Å, °).

Ni—S1	2.4119 (12)	S1—C2	1.830 (4)
Ni—S7	2.3917 (14)	S1—C9	1.805 (4)
Ni—O1	2.057 (3)	S7—C6	1.812 (4)
Ni—O2	2.086 (3)	S7—C8	1.827 (4)
Ni—N4	2.141 (4)	O1—C14	1.231 (5)
Ni—N13	2.073 (3)	O2—C18	1.232 (5)
S1—Ni—S7	87.66 (5)	O2—Ni—N13	88.61 (12)
S1—Ni—O1	91.47 (8)	N4—Ni—N13	94.77 (12)
S1—Ni—O2	89.78 (8)	Ni—S1—C2	96.27 (12)
S1—Ni—N4	86.83 (8)	Ni—S1—C9	100.88 (14)
S1—Ni—N13	178.23 (11)	C2—S1—C9	102.67 (19)
S7—Ni—O1	176.09 (9)	Ni—S7—C6	93.35 (14)
S7—Ni—O2	93.46 (8)	Ni—S7—C8	103.56 (13)
S7—Ni—N4	87.46 (9)	C6—S7—C8	103.13 (19)
S7—Ni—N13	93.17 (9)	Ni—O1—C14	129.2 (2)
O1—Ni—O2	90.35 (11)	Ni—O2—C18	127.2 (3)
O1—Ni—N4	88.68 (12)	Ni—N4—C3	106.5 (2)
O1—Ni—N13	87.81 (11)	Ni—N4—C5	112.5 (2)
O2—Ni—N4	176.45 (10)	Ni—N13—C12	117.4 (2)

The two MeCN solvent molecules were affected by disorder. In one molecule, the components were each half-occupied while the other clearly had major and minor occupancies of 0.694 (19) and 0.306 (19), respectively. Restraints were applied to the C—C, C≡N and 1,3-C···N distances. Restraints for planarity, local C_{2v} symmetry and similarity were applied to and between the phenyl rings. Methyl H atoms were located from ΔF syntheses while all other H atoms were placed geometrically. Methyl H atoms were refined as part of rigid rotating groups, with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. Other H atoms were refined using a riding model, with N—H = 0.92 Å, C—H(sp^2 and aryl) = 0.95 and C—H(methylene) = 0.99 Å, and with $U_{iso}(H) = 1.2U_{eq}(N,C)$. The maximum electron-density peak lies 1.25 Å from atom C18.

Data collection: *Stadi*-4 (Stoe & Cie, 1996); cell refinement: *Stadi*-4; data reduction: *X-RED*32 (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *PLATON*.

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