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Bis(tetraethylammonium) bis[*N*,*N*′-bis(4-methylbenzothiazol-2-yl)pyridine-2,6-dicarboxamidato(2−)]nickel(II) hemihydrate

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.052
wR factor = 0.140
Data-to-parameter ratio = 15.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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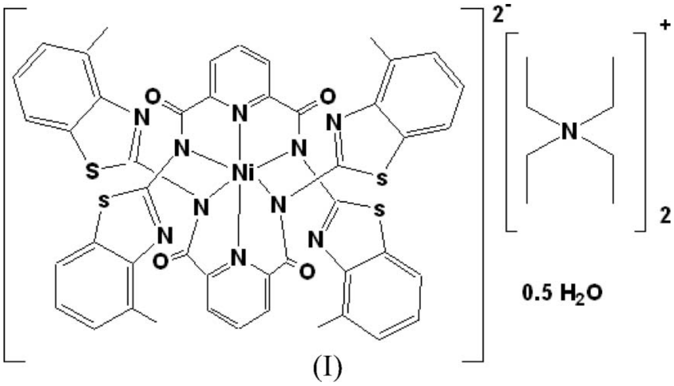
In the anion of the title compound, $(C_8H_{20}N)_2[Ni(C_{23}H_{15}N_5O_2S_2)_2]\cdot0.5H_2O$, the central Ni^{II} atom is in an octahedral environment, with four deprotonated amide N atoms in the equatorial plane and two pyridine N atoms in the axial positions. In the crystal structure, intermolecular O—H···O, C—H···O and C—H···S hydrogen bonds link the molecules into a three-dimensional supramolecular framework.

Comment

Transition complexes with non-macrocyclic chelating ligands containing the amide functionality have drawn much attention in past years (Bruckner *et al.*, 2000). Some investigations have revealed that deprotonated N atoms of organic amides, being anionic in nature, are capable of stabilizing the trivalent oxidation state to a considerable extent (Patra & Mukherjee, 1999; Singh *et al.*, 2003). Recently, there has been an increasing interest in the chemistry of deprotonated carboxamide toward transition metal ions as a result of their striking catalytic activities (Qi *et al.*, 2003). In order to develop further the coordination chemistry of pyridine amide ligands with transition metal ions, we have synthesized an Ni^{II} complex based on *N*,*N*′-bis(4-methylbenzothiazol-2-yl)pyridine-2,6-dicarboxamide, (L^{2-}).



(I)

In the IR spectrum of the title complex, (I), the absence of ν(NH) (3170 cm^{-1}) confirms that the ligands are coordinated to Ni^{II} ions in the deprotonated form. The C═O stretching vibration (1632 cm^{-1}) is lower than that of the free ligand (1655 cm^{-1}). Such behavior is also observed in another deprotonated amide complex (Liu *et al.*, 2004).

In (I), the bond lengths and angles are generally within normal ranges (Allen *et al.*, 1987). The structure of the anion of the complex is shown in Fig. 1. The Ni atom is coordinated by four deprotonated amide N atoms in the equatorial plane and two pyridyl N atoms in the axial positions. The dihedral

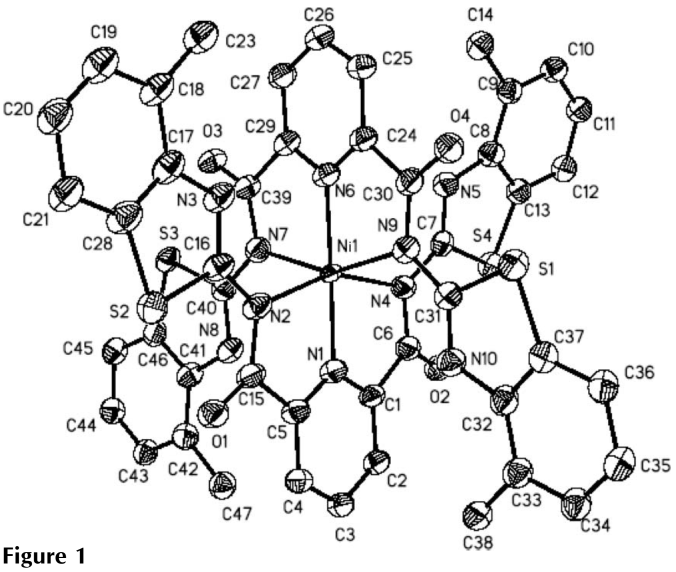


Figure 1

The structure of the anion in the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted.

angle between the two planar units N1/N2/N4/Ni1 and N6/N7/N9/Ni1 is 87.1 (8)°. The geometry of the NiN6 coordination is appreciably compressed octahedral. The bond angles involving the chelation obviously deviated from 90°, which is presumably due to the formation of the five-membered chelate rings. The average Ni—N_{amide} [2.179 (3) Å] bond is longer than that of Ni—N_{py} [1.970 (3) Å], which is the result of the steric predominance over electronic effects in (I).

In the crystal structure, intermolecular O—H···O, C—H···O and C—H···S hydrogen bonds link the ions into a three-dimensional supramolecular framework.

Experimental

The ligand H_2L was synthesized according to the literature method (Liu *et al.*, 2004). The ligand H_2L (460 mg, 1 mmol) and NaH (48 mg, 2 mmol) in DMF (15 ml) were added to a solution of $NiCl_2·6H_2O$ (237 mg, 1 mmol) in DMF (5 ml). The resulting solution was magnetically stirred for 15 min, and then excess $[Et_4N]Cl.xH_2O$ was added and the mixture was stirred for about 1 h. Exposure of this solution to air for a week gave light-yellow single crystals, suitable for structural studies (yield 470 mg, 75.60%).

Crystal data

$(C_8H_{20}N)_2[Ni(C_{23}H_{15}N_5O_2S_2)_2]$·0.5$H_2O$
M_r = 1243.28
Monoclinic, $P2_1/n$
a = 14.4474 (15) Å
b = 19.514 (2) Å
c = 21.771 (2) Å
β = 97.642 (2)°
V = 6083.2 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.52 mm^{-1}
T = 291 (2) K
0.3 × 0.25 × 0.2 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.86, T_{max} = 0.90
32320 measured reflections
11915 independent reflections
10496 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.140
S = 0.94
11915 reflections
769 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Table 1

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5B···O2^{i}	0.85	2.14	2.900 (6)	150
C12—H12···O2^{ii}	0.93	2.52	3.340 (4)	147
C56—H56B···O1^{iii}	0.97	2.27	3.214 (5)	164
C57—H57A···O3^{iv}	0.96	2.59	3.392 (4)	141
C62—H62A···S3^{iv}	0.97	2.78	3.461 (4)	128

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

H atoms were positioned geometrically with O—H = 0.85 Å, and C—H = 0.93, 0.97 and 0.96 Å, for aromatic, methylene and methyl H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C,O)$, where x = 1.2 for aromatic and methylene H, and x = 1.5 for all other H atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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