Crystal structure of *tetra*-aqua-*bis*-(pyridine-4-carboxamide-*N*)-nickel(II) 1,5-naphthalenedisulfonate-isonicotinamide-water (1:2:4), $[Ni(H_2O)_4(C_6H_6N_2O)_2][C_{10}H_6S_2O_6]\cdot 2C_6H_6N_2O\cdot 4H_2O$, $C_{34}H_{46}N_8NiO_{18}S_2$

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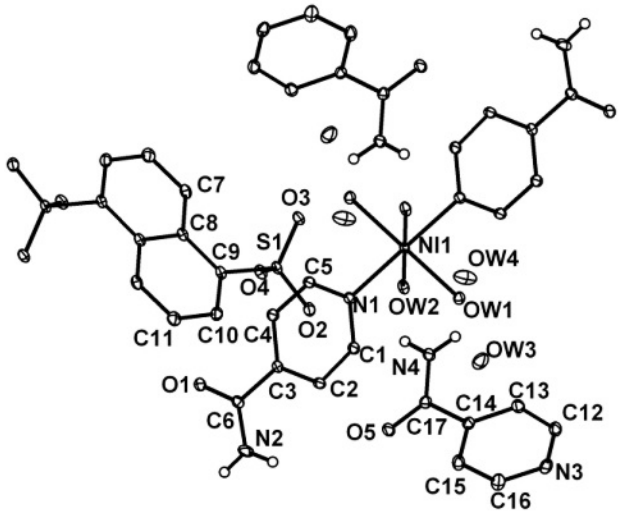

Abstract

$C_{34}H_{46}N_8NiO_{18}S_2$, triclinic, $P\bar{1}$ (no. 2), a = 10.345(7) Å, b = 10.864(5) Å, c = 10.895(3) Å, α = 70.87(3)°, β = 74.96(4)°, γ = 78.21(5)°, V = 1107.6 Å^3, Z = 1, $R_{gt(F)}$ = 0.0453, $wR_{ref(F^2)}$ = 0.1241, T = 298 K.

Table 1. Data collection and handling.

Crystal:	green blocks, size 0.20×0.40×0.50 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	22.25 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	134.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7680, 3840
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3665
$N(param)_{refined}$:	287
Programs:	SHELX [7]

Source of material

Isonicotinamide (0.048 g, 0.4mmol) was added with constant stirring to an aqueous solution (20 ml) of $Ni(CH_3COO)_2$ (0.035 g, 0.2mmol). The solution was then treated with disodium naphthalene-1,5-disulfonate (0.66 g, 0.2mmol). Green crystals of the title complex were collected after 4 days. (40% yield based on Ni.)

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.93 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The O-bound H atoms were located in difference maps and refined as riding in their as-found relative positions with U_{iso}(H) = 1.2U_{eq}(O).

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Discussion

The rational control of molecular self-assembly into ordered solid-state networks with a desired arrangement and dimensionality is a challenge for chemists. Many attempts to control the structures in the solid state have been made via hydrogen-bonding and/or other noncovalent interactions [1-4]. As an excellent hydrogen donor and hydrogen acceptor, INA (isonicotinamide) has been applied in constructing supramolecular architectures, such as ribbons, sheets, and rectangular nets [2-4]. The sulfonate group is an excellent hydrogen acceptor candidate and has been widely used by Ward and co-workers in their guanidinium sulfonate inclusion family [1,5,6]. As part of our research in this area, we report here the crystal structure of the title compound. The asymmetric unit contains one Ni atom, two INA ligands, four water molecules, and half of the 1,5-NDS (naphthalene-1,5-disulfonate) anion. The Ni atom occupies an inversion centre and is coordinated by four oxygen atoms of two symmetry related water ligands (Ni–O1 = 2.0594(2) and Ni-O2 = 2.0770(2) Å) and two nitrogen atoms (Ni–N = 2.0920(2) Å of two symmetry related INA ligands, showing a lightly distorted octahedral geometry. The bond angles around the Ni atom at the equatorial plane defined by Ow1, Ow2 and Ow1' and Ow2' sum to 360° within experimental error, showing that they are coplanar. The 1,5-NDS has an inversion centre at the midpoint of the central C–C bond, and does not participate in coordination. The INA ligand has two different forms. One form of INA ligand coordinates to the Ni atom, the other is guest. A pair of isonicotinamide ligands coordinates through the pyridine nitrogen atom in trans-positions. Consequently, the two amides are oriented in a linear fashion pointing in opposite directions. The complex cations and 1,5-NDS anions align in a neat alternating mode and interact with each other via N–H···O and O–H···O hydrogen bonds between the sulfonate groups and coordinated water molecules, resulting in the formation of infinite chains. Adjacent chains are linked by hydrogen bonds formed between the sulfonate groups and amide forming two dimensional extended sheets. The remaining NH proton on the amide group forms hydrogen bonds with sulfonate O atoms from neighboring sheets, leading to a three dimensional network with channels. The guests of INA ligands are located in the channels, and form the hydrogen bonds with the coordinated water molecules and sulfonate oxygen atoms.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.5434	0.2572	0.5015	0.027
H(1B)	2*i*	0.6309	0.3173	0.4065	0.027
H(2C)	2*i*	0.3451	0.3684	0.7152	0.030

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2D)	2*i*	0.2609	0.4584	0.6395	0.030
H(3A)	2*i*	0.1483	–0.0012	0.9857	0.064
H(3B)	2*i*	0.0675	0.1026	1.0041	0.064
H(4C)	2*i*	0.2680	0.2024	0.9208	0.066
H(4D)	2*i*	0.3676	0.2753	0.9425	0.066
H(2A)	2*i*	0.0189	0.6370	–0.0095	0.043
H(2B)	2*i*	0.0731	0.5321	0.0993	0.043
H(4A)	2*i*	0.5970	0.4557	0.0678	0.031
H(4B)	2*i*	0.6500	0.3403	0.1692	0.031
H(1)	2*i*	0.3033	0.3992	0.4064	0.031

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	2*i*	0.1687	0.4621	0.2529	0.030
H(4)	2*i*	0.2906	0.8183	0.1271	0.029
H(5)	2*i*	0.4223	0.7455	0.2839	0.028
H(7)	2*i*	0.0513	0.9157	0.7422	0.029
H(10)	2*i*	0.0179	0.6998	0.4480	0.031
H(11)	2*i*	–0.0337	0.8691	0.2632	0.036
H(12)	2*i*	0.6698	–0.0874	0.3562	0.036
H(13)	2*i*	0.6898	0.1236	0.2214	0.033
H(15)	2*i*	0.2899	0.1765	0.2387	0.039
H(16)	2*i*	0.2825	–0.0332	0.3789	0.045

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	1*h*	½	½	½	0.0160(3)	0.0167(3)	0.0179(3)	–0.0024(2)	–0.0063(2)	–0.0007(2)
S(1)	2*i*	0.07222(4)	0.68176(4)	0.69011(4)	0.0156(3)	0.0217(3)	0.0207(3)	–0.0017(2)	–0.0060(2)	0.0006(2)
O(1)	2*i*	0.1219(2)	0.8146(1)	–0.0003(1)	0.0320(8)	0.0220(8)	0.0308(8)	–0.0024(6)	–0.0163(6)	–0.0013(6)
O(2)	2*i*	0.0915(1)	0.5643(1)	0.6476(2)	0.0247(7)	0.0235(7)	0.0347(8)	–0.0009(6)	–0.0105(6)	–0.0039(6)
O(3)	2*i*	0.1963(1)	0.7077(1)	0.7126(1)	0.0171(7)	0.0284(8)	0.0273(7)	–0.0023(5)	–0.0080(5)	–0.0023(6)
O(4)	2*i*	–0.0403(1)	0.6819(1)	0.8035(1)	0.0201(7)	0.0308(8)	0.0207(7)	–0.0045(6)	–0.0042(5)	0.0014(6)
O(5)	2*i*	0.4091(2)	0.3599(1)	0.0530(2)	0.0322(8)	0.0239(8)	0.0382(8)	–0.0066(6)	–0.0190(7)	0.0025(6)
OW(1)	2*i*	0.5565(1)	0.3279(1)	0.4478(1)	0.0211(7)	0.0192(7)	0.0221(7)	–0.0033(5)	–0.0028(5)	–0.0017(5)
OW(2)	2*i*	0.3402(1)	0.4126(1)	0.6382(1)	0.0183(7)	0.0251(7)	0.0240(7)	–0.0018(5)	–0.0040(5)	0.0018(6)
OW(3)	2*i*	0.1550(2)	0.0718(2)	0.9822(2)	0.0312(9)	0.0315(9)	0.094(2)	–0.0099(7)	–0.0029(9)	–0.019(1)
OW(4)	2*i*	0.3369(2)	0.2496(2)	0.8834(2)	0.071(1)	0.066(1)	0.0304(9)	–0.047(1)	–0.0168(9)	0.0087(9)
N(1)	2*i*	0.3759(2)	0.5655(2)	0.3611(2)	0.0199(8)	0.0210(8)	0.0207(8)	–0.0029(6)	–0.0058(6)	–0.0038(6)
N(2)	2*i*	0.0664(2)	0.6125(2)	0.0505(2)	0.049(1)	0.032(1)	0.031(1)	–0.0177(9)	–0.0274(9)	0.0073(8)
N(3)	2*i*	0.4750(2)	–0.0808(2)	0.3806(2)	0.033(1)	0.0191(9)	0.0322(9)	–0.0055(7)	–0.0026(7)	–0.0006(7)
N(4)	2*i*	0.5922(2)	0.3769(2)	0.1195(2)	0.0293(9)	0.0221(8)	0.0257(9)	–0.0065(7)	–0.0122(7)	0.0017(7)
C(1)	2*i*	0.3006(2)	0.4845(2)	0.3496(2)	0.027(1)	0.020(1)	0.029(1)	–0.0054(8)	–0.0126(8)	0.0008(8)
C(2)	2*i*	0.2192(2)	0.5215(2)	0.2574(2)	0.024(1)	0.023(1)	0.030(1)	–0.0069(8)	–0.0118(8)	–0.0037(8)
C(3)	2*i*	0.2138(2)	0.6485(2)	0.1719(2)	0.0182(9)	0.0215(9)	0.0184(9)	–0.0012(7)	–0.0050(7)	–0.0040(7)
C(4)	2*i*	0.2915(2)	0.7326(2)	0.1829(2)	0.027(1)	0.020(1)	0.025(1)	–0.0059(8)	–0.0103(8)	0.0005(8)
C(5)	2*i*	0.3705(2)	0.6880(2)	0.2777(2)	0.025(1)	0.022(1)	0.025(1)	–0.0059(8)	–0.0104(8)	–0.0030(8)
C(6)	2*i*	0.1287(2)	0.6978(2)	0.0677(2)	0.022(1)	0.025(1)	0.0193(9)	–0.0041(8)	–0.0060(7)	–0.0030(8)
C(7)	2*i*	0.0322(2)	0.9821(2)	0.6673(2)	0.025(1)	0.027(1)	0.0171(9)	0.0017(8)	–0.0077(7)	–0.0024(8)
C(8)	2*i*	0.0151(2)	0.9487(2)	0.5575(2)	0.0152(9)	0.025(1)	0.0174(9)	–0.0004(7)	–0.0035(7)	–0.0031(8)
C(9)	2*i*	0.0280(2)	0.8157(2)	0.5544(2)	0.0161(9)	0.023(1)	0.0189(9)	–0.0001(7)	–0.0047(7)	–0.0019(7)
C(10)	2*i*	0.0099(2)	0.7869(2)	0.4471(2)	0.029(1)	0.023(1)	0.025(1)	0.0006(8)	–0.0085(8)	–0.0063(8)
C(11)	2*i*	–0.0209(2)	0.8891(2)	0.3355(2)	0.036(1)	0.033(1)	0.023(1)	0.0008(9)	–0.0115(8)	–0.0094(9)
C(12)	2*i*	0.5926(2)	–0.0329(2)	0.3331(2)	0.029(1)	0.024(1)	0.035(1)	–0.0029(8)	–0.0097(9)	–0.0013(9)
C(13)	2*i*	0.6059(2)	0.0935(2)	0.2512(2)	0.023(1)	0.026(1)	0.032(1)	–0.0058(8)	–0.0072(8)	–0.0024(9)
C(14)	2*i*	0.4915(2)	0.1747(2)	0.2145(2)	0.025(1)	0.020(1)	0.0227(9)	–0.0035(8)	–0.0050(8)	–0.0043(8)
C(15)	2*i*	0.3684(2)	0.1253(2)	0.2623(2)	0.024(1)	0.024(1)	0.043(1)	–0.0032(8)	–0.0050(9)	–0.0005(9)
C(16)	2*i*	0.3654(2)	–0.0013(2)	0.3454(3)	0.025(1)	0.028(1)	0.049(1)	–0.0072(9)	0.001(1)	–0.000(1)
C(17)	2*i*	0.4956(2)	0.3120(2)	0.1226(2)	0.024(1)	0.021(1)	0.0219(9)	–0.0038(7)	–0.0039(7)	–0.0035(8)

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